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MBR activated sludge filterability characterization in cross flow filtration

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Dissertação apresentada na Faculdade de Ciências e Tecnologia da Universidade Nova de Lisboa para a obtenção do grau de Mestre em Engenharia do Ambiente, perfil Sanitária

Orientador científico: Professora Doutora Leonor Amaral

Lisboa, 2009

Like our ancestors needed the Sea to reach great achievements, without fear of the unknown. Our generation and the following also depend on the Sea for their development and well being.

I dedicate my Master Thesis to my parents, my girlfriend and my family

Acknowledgements

The research project that supports this thesis was carried out at the Sanitary Department of Civil Engineering Faculty at TU Delft University, from February to July 2009.

Through this University it was possible to perform a practical work in a wastewater treatment plant (WWTP) in Heenvliet and I would like to thank André Westerdijk the WWTP responsible, for all the support in the plant.

I would like to express my gratitude to Leonor Amaral, my supervisor in Lisbon and to Adrien Moreau, my supervisor in Delft, for all the support and their availability.

I also would like to express my appreciation to everyone in the Sanitary Department of TU Delft for their friendship and daily support, especially to Maria Lousada, Tony Schuit, Patrick Andeweg and Mike Hubert.

Special thanks to my parents to offer me this important opportunity in my student life, to my girlfriend and all my family for the support.

RESUMO

Comparando com os métodos tradiconais de lamas activadas, é a fiabilidade de funcionamento dos biorreactores de membrana (MBR) e a sua capacidade de obtenção de resultados bastante satisfatórios relativamente às exigências de tratamento de águas residuais o que torna esta tecnologia tão promissora.

No entanto, a separação fase sólida - fase líquida que integra o tratamento biológico, por se tratar de um sistema físico e químico induz um fenómeno chamado *fouling* - fenómeno que se baseia no entupimento da membrana, que obriga a incluir no processo de tratamento, custos adicionais associados ao aumento do consumo de energia e a lavagens físicas e químicas periódicas.

Na presente tese é realizado um enquadramento da utilização da tecnologia MBR e apresentado o estado actual dos conhecimentos referentes a esta tecnologia.

Os trabalhos de investigação desenvolvidos tiveram uma componente eminentemente experimental, tendo sido utilizada uma instalação de caracterização de filtração (DFCi) de lamas activadas, desenvolvida pela Delft *University of Technology* (Evenblij *et al.*, 2005) na Holanda. Na ETAR de Heenvliet, também na Holanda, cujo tratamento inclui um sistema convencional de lamas activadas em arejamento prolongado e um sistema MBR, foram realizados ensaios de filterabilidade, com controlo de sólidos suspensos, colóides e solutos constituintes das lamas activadas do sistema de MBR através das seguintes análises laboratoriais: sólidos suspensos totais, sólidos suspensos voláteis, carência química de oxigénio, contagem de partículas nos intervalos 0.4-5.0 µm e carbono orgânico total.

Foi estudada a influência da velocidade de atravessamento das lamas activadas em membranas com filtração de fluxo cruzado (onde a água residual percorre a membrana paralelamente à sua superfície) e também foi realizada uma monitorização in situ da filterabilidade das lamas activadas do sistema MBR da ETAR de Heenvliet.

Os resultados obtidos nas análises relativas à monitorização da filterabilidade das lamas activadas do sistema MBR da ETAR de Heenvliet mostraram correlações fortes do tratamento biológico e das variações sazonais com as características e filterabilidade das lamas activadas. Em relação à influência da velocidade de atravessamento das lamas activadas nas membranas com filtração de fluxo cruzado, as velocidades de atravessamento acima de 1m/s (consideradas as mais elevadas, nesta investigação) apresentaram as melhores correlações entre a filterabilidade das lamas activadas e as respectivas características analisadas.

ABSTRACT

The reliability of MBR operation and its capability to produce favorable results as regards water treatment, in comparison with conventional activated sludge systems, makes this technology so promising.

However as the MBR treatment process is a physical chemical process involving filtration and biological treatment, it leads to the phenomena of fouling – resulting in membranes becoming obstructed, requiring more energy and physical chemical cleaning, thus increasing the additional associated costs.

In this thesis, a framework analysis of MBR technology uses is undertaken and the current state of the art regarding this technology.

This research included an important experimental component, with the Delft Filtration Characterization method (DFCm) developed by TU Delft (Evenblij *et al.*, 2005) for activated sludge filterability measurements, developed by Delft University of Technology in the Netherlands. Activated sludge filterability was compared with subsequent laboratory analyses: chemical oxygen demand, total organic carbon, total suspended solids, volatile suspended solids and particle counts in 0.4-5.0µm range. The aim of these analyses was a fractionation of sludge samples in suspended solids, colloids and solute. The sludge samples were collected on MBR full-scale in Heenvliet Wastewater treatment plant (WWTP), also in the Netherlands, where the treatment process also includes a conventional activated sludge system (oxidation ditch activated sludge).

The influence of different cross flow velocities on sludge filterability in cross flow filtration was performed, using in-situ monitoring of Heenvliet WWTP.

The results obtained in this study relating to monitoring of Heenvliet WWTP, showed a strong correlation between the activated sludge characteristics and the filterability.

Regarding the influence of different cross flow velocities on sludge filterability in cross flow filtration, velocities above 1m/s (considered as high velocity in this research), showed the strongest correlations between the filterability of activated sludge and its respective fractionation compounds (suspended solids, colloids and solutes).

LIST OF SYMBOLS

Symbol - Meaning

ASP - Activated sludge process

BOD - Biochemical oxygen demand

COD - Chemical oxygen demand

CFV - Cross Flow Velocity

ΔR20 - Additional resistance when 20 L/m^2 of permeate have been extracted

DFCi - Delft filtration characterization installation

DFCm - Delft filtration characterization method

DWF – Dry weather flow

F/M - Food to microorganism ratio

FS - Flat sheet

HF - Hollow fiber

HRT - Hydraulic retention time

iMBR - Immersed membrane bioreactor

LMH - Liters per square meter per hour - L/ (m^2.h)

MLSS - Mixed liquor suspended solids

MF - Microfiltration

MBR - Membrane bioreactors

MT - Membrane tank

NF - Nanofiltration

PLC - programmable logic controller

RO - Reverse osmosis

sMBR - Sidestream membrane bioreactor

SMP - Soluble microbial products

SRT -Sludge retention time

SVI - Sludge volume index

TMP - Trans-membrane pressure

TSS - Total suspended solids

uCR - Cross-flow velocity

TOC - Total organic carbon

TSS - Total suspended solids

UF - Ultrafiltration

VSS - Volatile suspended solids

UF - Ultrafiltration

WWTP - Wastewater treatment plant

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1 – INTRODUCTION

1.1 - General overview

Nowadays a sustainable water use becomes more important than ever. As the climate changes are accelerating and considering the water shortage in southern European countries in a near future the situation will get worse. So an efficient water reuse is undoubtedly one of the answers to this problem.

Considering this situation, the most efficient and effective technologies for wastewater treatment and reuse are of increased interest in this context.

One of these technologies is the Membrane Bioreactor (MBR) which allows the separation of treated wastewater from the active biomass, with a solid-liquid separation by membrane filtration.

1.2 - Objective

The MBR process is considered an advanced wastewater treatment technology, which permits treatments of both municipal and industrial wastewater. However as the activated sludge contains mostly suspended particles, during filtration occurs a phenomena called fouling, blocking the membrane pores.

The membrane fouling phenomena have been investigated by many research groups around Europe (and the rest of the world). This thesis describes the work done by the author in a research group of water management in the Civil Engineering and Geosciences building, on TU Delft in the department of water management, section of Sanitary Engineering in the Netherlands. It was supervised by the engineer Adrien Moreau and included in his PhD research, which deals with the optimization full-scale MBR, under the supervision of Professor ir. Jaap van der Graaf.

This research is included in the framework of a Master Thesis of the Environmental Engineering course at the Faculty of Sciences and Technology from the New University of Lisbon. In Portugal this work was supervised by Professor Leonor Miranda Monteiro do Amaral.

The practical work consisted in two important phases. A regular monitoring of activated sludge filterability collected on the membrane tank of MBR system on Heenvliet Wastewater treatment plant in Netherlands and the influence of different cross flow velocity (CFV) on tubular membrane fouling, both analyses were performed with Dfci (Delft filtration characterization installation). It was possible to expand this research with specific laboratory analyses of the activated sludge characteristics. These laboratory experiments focused on activated sludge samples fractionation in colloids, suspended solids and solutes (parameters that influence fouling phenomena). So it was possible to specify the influence of different cross flow velocities with the comparison of the activated sludge fractions and the activate sludge filterability.

The final goal is to provide practical and useful advices for MBR full-scale operation.

1.3 - Organization of the Thesis

In Chapter 2 a literature review with the MBR state of the art is given, where the general terms and concepts involving wastewater treatment concepts and membrane filtration technology characteristics are described.

Chapter 3 gives general information about Heenvliet WWTP, an explanation of Dfcm (Delft filtration characterization method) and the practical methodology followed on this thesis.

The methodology followed on the research of this thesis and the results discussion are presented more specifically in Chapter 4, where the general measuring protocol is described considering the materials and methods for each laboratory analyses applied and the results obtained with the respectively interpretations for each result.

The general conclusions are in chapter 5 and recommendations for further research are given in chapter 6.

2 – LITERATURE REVIEW

2.1 - Activated sludge

The follow activated sludge process description was based in Metcalf &Eddy (2003) description mentioned by Brandão (2009).

The activated sludge process is a suspended growth process of wastewater treatment where the microorganisms (mainly bacteria) responsible for the organic matter degradation are maintained in liquid suspension by appropriate aerobic mixing methods.

Thanks to experiences developed by Arden and Locket around 1912-1914, was discovered the activated sludge process (ASP). They found that with aeration process applied to retained wastewater, they could create an activated mass of microorganisms with aerobic stabilization of organic matter present in the wastewater.

The ASP is a suspended enlargement process of wastewater treatment where the microorganisms responsible for treatment are maintained in liquid suspension by appropriate mixing methods; this mixture is usually mentioned as mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS).

Basically it is composed by a bioreactor with aeration system, where the biomass stays in suspension, a liquid-solids separation, which is generally in sedimentation tanks, and a recirculation process that allow the solids removed from the liquid-solids separation, return to the reactor to maintain stabilized the ratio microorganisms and organic matter (F/M). In sedimentation tanks, the process occurs by gravity due to the formation of flocculent settleable solids sized between the ranges of 50 to 200µm.

On wastewater treatment plants before the ASP the wastewater must suffer a preliminary treatment which removes the coarse solids, grit and grease and a primary treatment (frequently omitted for applications from smaller-sized communities, and in areas of the world that have hot climates) to remove part of the suspended solids and organic matter from the wastewater. Pretreatment stage (preliminary treatment) is a very important stage in the wastewater treatment because with the proper functioning is possible increase the effectiveness of a later, more specific treatment and to prevent damages in equipment.

The active biological material produced by activated sludge is responsible for removing biodegradable organics, pathogens and nutrients like nitrogen and phosphorous. The biodegradable organics are mainly composed by proteins, carbohydrates and fats, most commonly measured in terms of biochemical oxygen demand (BOD) and chemical oxygen demand (COD). The nitrogen remove method is executed by different bacteria and is based on the oxidization of ammonia nitrogen (nitrification), converted into nitrite and nitrate follow by a reduction (denitrification) to gaseous nitrogen dispersed into the atmosphere. For phosphorous removal it is induced bacteria growth (with specific biological process) capable of phosphorous accumulating followed by a sedimentation process.

For the ASP design the most critical parameter is the solids retention time (SRT) because it affects the treatment process performance, aeration tank volume, sludge production and oxygen requirements.

Another important parameter in the ASP design is the food to microorganism ratio (F/M) which represents the substrate available for the biomass, usual values for the BOD. F/M ratio reported in the literature vary from 0.04 (g substrate/g biomass. day) for extended aeration processes to 1.0 (g substrate/g biomass. day) for high rate processes.

The final stage in the ASP is the separation of the effluent from the biomass using traditionally clarifier tank by gravity. The parameter used to design the clarifier tank involves the measurement of the settling characteristics of the mixed liquors which is the sludge volume index (SVI in mL/g), which corresponds to the volume of 1 g of sludge after 30 min of settling in 1 liter cylinder.

The removed sludge in waste water treatment plants are the largest constituent removed by treatment. The principal methods used for solids processing are thickening (concentration), digestion, and conditioning, followed by the removal moisture from solids and finally dewatering and drying.

2.2 - MBR State of the Art

2.2.1 - Membrane Bioreactor origins

In 1922 Zsigmondy patented the microporous membrane. And the first microfiltration membrane being commercialized was in 1929 by the Sartorius Werke GmbH in Gottingen, Germany (Zsigmondy, (1922), patented rights, cited by Belfort *et al.* (1994)). During the World War II, Germany used microfiltration membranes, to rapidly guarantee water supplies in bombed-out German cities (Belfort *et al.,* 1994).

Then in the United States and Japan this technology saw an important commercial and process development. During 1980's Zenon Environmental became one of the most important companies in United States and in Japan the agricultural machinery company Kubota was one of the most important, both developing MBR technology (Judd, 2006). Nowadays there are a lot of new membranes companies spread around the world, and the membrane market offers many technologies for each specific use in water and wastewater treatment.

2.2.2 - Membrane Bioreactor

A membrane bioreactor is a technology which combines the activated sludge process (bioreactor) with a membrane separation step. So it replaces and in some cases complements the solids separation function of secondary clarification and effluent filtration (Metcalf & Eddy, 2003). Basically a membrane is a material that allows some physical or chemical components to pass through more readily than others. It is perm-selective, which means that it is more permeable to those constituents passing trough it (which then became permeate) than those which are rejected by it (which form the concentrate), (Judd, 2006).

The membrane support facility require equipment, such as pumps, for activated sludge circulation and permeate extraction for constant flux filtrations, chemical storage tanks, chemical feed pumps, air-scour systems and a back-pulse water flushing system. The constituents in the feed-water tend to accumulate on the membranes increasing the inside pressure. Thus, the membrane flux starts to decrease and the trans-membrane pressure increases. At a certain level of decreasing performance, the membranes must be backwashed and/or chemically cleaned (Metcalf & Eddy, 2003).

Following are defined the parameters of membrane filtration:

The flux, J, is the quantity of material passing through the membrane surface per time. It can be also called as permeate or filtration velocity and it can be calculated by Darcy´s law (Lojkine *et.al,* 1992) (equation 2.3).

$$J = \frac{\Delta P}{R_t \times \eta} \qquad \text{Eq.2.3}$$

With:

J = Permeation flux [L/m^2.h or LMH] or [m/s]

η = Viscosity (Kg/m.s^2)

ΔP = Trans-membrane pressure [Pa] or [bar]

Rt = Total filtration resistance [m^{-1}]

In the MBR process the driving force for the filtration is trans-membrane pressure (TMP), which consists in the difference between in and out pressure, feed stream pressure and permeate pressure respectively.

As the trans-membrane pressure increases during the filtration process, the membrane applies a physical resistance which the total resistance is the sum of the resistance of the fouling layer and the resistance offered by the membrane when it is clean (equation 2.4)

$$\mathrm{Rt} = \mathrm{Rm} + \mathrm{Rf} \qquad \text{Eq.2.4}$$

With:

Rt = Total filtration resistance

Rm = Clean membrane resistance

Rf = Fouling resistance

The permeability, which is inversely proportional to total filtration resistance, is a common parameter to characterize the membrane performance. It can be calculated through equation 2.5.

$$\mathrm{P} = \frac{J}{TMP} \qquad \text{Eq.2.5}$$

Where:

P = Permeability	[$Lm^{-2}h^{-1}bar^{-1}$]
J =Permeation flux	[$Lm^{-2}h^{-1}$]
TMP = Trans-membrane pressure	[Pa], or [bar]

There are two membrane modules designs with different pressure requirements (Figure 2.1):

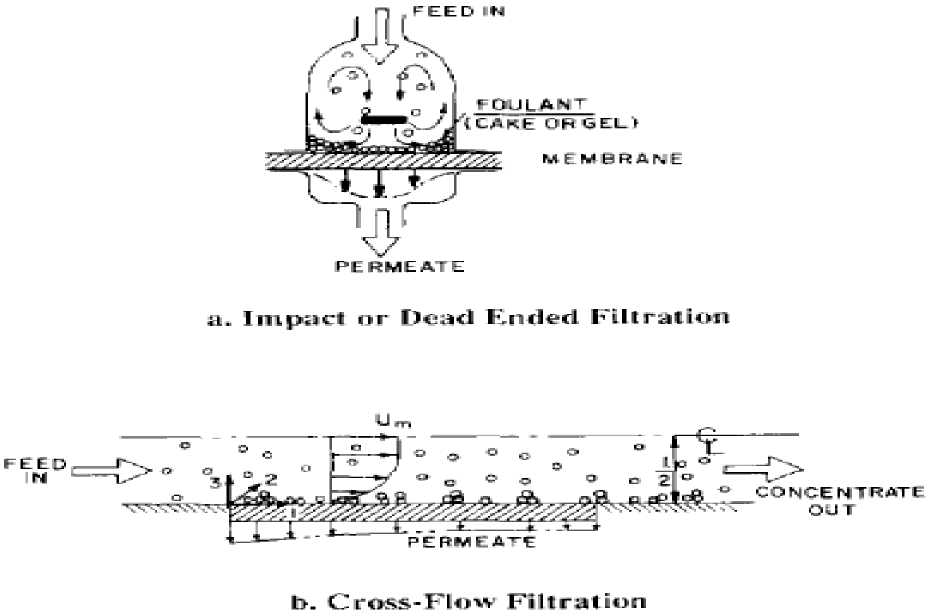

Figure 2.1 - Schematic showing the feed flowing perpendicular and tangential in (a) dead-end and (b) cross-flow filtration, respectively (Belfort et al., 1994).

The “dead end” filtration where the flow goes strictly perpendicular to the membrane, with one inlet port is simpler and is normally used only in laboratory applications (few litters only). And the “cross-flow” filtration where the flow is tangentially to the membrane, with inlet and outlet ports.

In the cross-flow MBR there are two configurations, the immerse membrane bioreactor (iMBR) where the membrane is inside the sludge tank. This requires less energy than the side stream membrane bioreactor (sMBR) which consumes more energy to circulate the activated sludge to the membrane module which is placed outside the sludge tank (Metcalf & Eddy, 2003) (Figure 2.2).

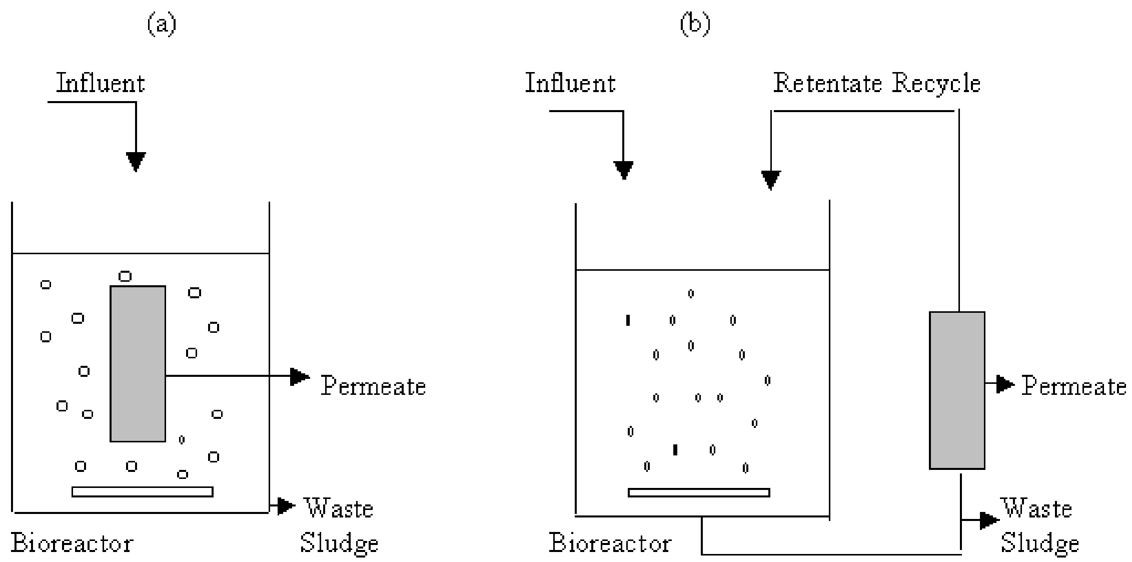

Figure 2.2 - Schematic of the immersed membrane (a) and external membrane (b) (Melin et al., 2006).

2.2.3 - Membrane Fouling

In this thesis the IUPAC (International Union of Pure and Applied Chemistry) fouling definition was considered: "Process resulting in loss of performance of a membrane due to deposition of suspended or dissolved substances on its external surfaces, at its pore openings, or within its pores" (Koros, 1996).

Recently many researchers like Itonaga *et al.* (2004) mentioned by Le-Clech *et al.* (2006) associate the EPS (extracellular polymeric substances) and SMP (soluble microbial products) to fouling. EPS and SMP are substances produced by microorganisms that are released in the liquid phase of the activated sludge. These substances can be quantified by COD (chemical oxygen demand) and TOC (total organic carbon) parameters (Evenblij *et al.,* 2005).

The particles concentration, expressed as MLSS (mixed liquor suspended solids), which influences the sludge viscosity (Rosenberger *et al.*, 2006), is considered to have an impact on fouling depending on the MLSS concentration (*Rosenberger et al.*, 2005). The viscosity of a fluid is a measure of its resistance to tangential or shear stress (Metcalf & Eddy, 2003).

The MBR technology uses a solid-liquid separation process in which the activated sludge characteristics are not always the same. During the cross-flow filtration process a gradual deposition of small particles (salts, small organic molecules, colloids, etc) occurs in the membrane, forming a layer in the membrane filtration area which originates fouling (Belfort *et al.*, 1994).

Fouling can be characterized according to the nature of the constituent, the mechanism by which it operates, or by the strategy adopted to control it.

The fouling constituents could be:

- Particulates (inorganic or organic) can proceed as foulants according to their ability to blind or block the surface
- Organic dissolved components and colloids which can fix on the membrane surface by adsorption.
- Inorganic dissolved components and coagulant residuals which tend to precipitate on the membrane surface.
- Micro-biological organisms, which category covers vegetative matter such as algae and organisms like bacteria which can form colonies, causing bio-fouling.

Therefore the fouling occurs due to a combination of chemical and physical interactions.

2.2.3.1 - Fouling mechanisms

The mechanism of particulate fouling (Figure 2.3) is a progressive growth depending on the concentration of particles present in the feed, and the extent of time before action is taken to invert their effect.

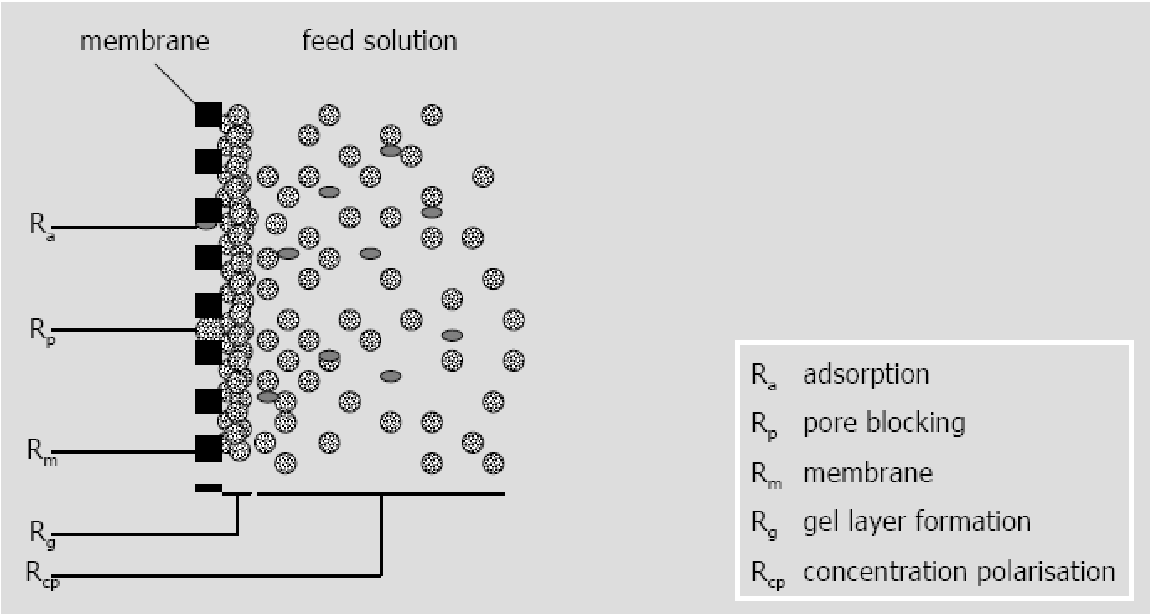

Figure 2.3 - Different fouling mechanisms in membrane cross-flow filtration (Evenblij, 2006).

First particles will begin to drop on the membrane surface, restricting the pore openings in different ways (pore blocking or pore adsorption, in (Figure 2.3). The next stage of particulate fouling involves the increase of a gel layer on the membrane surface, as additional particles continue to be deposited on the initial layer. As soon as the gel starts to gets bigger, it forms a cake layer that will influence transport and removal, improving removal efficiency, and protecting the surface from adsorptive fouling, but decreasing permeability (Wiesner *et al.,* 2005). Concentration polarization is the reversible build-up of dissolved or suspended solute near surface due a balance between the convective drag towards and through the membrane, reducing permeation flux (Belfort *et al*., 1994).

During the MBR wastewater treatment three main actions can be taken to avoid or reduce fouling phenomena:

- Prevention: backwash to remove the cake layer stuck on the membrane; air scour systems for improvement of mass transfer and transport, by increasing shear of the wastewater constituents. In addition forward flush to improve shear and remove build up particles concentration.
- Maintenance: Chemical wash used several times per day to once per week. Usually it is NaOH to combat organic fouling, acid citric to combat inorganic fouling and H_2O_2 to combat bio-fouling.
- Recovery: cleaning-in-place (CIP) used once per week up to several months. It is applied in extreme conditions of fouling, normally with chemicals addition. It consists of recirculation with heated water and chemicals (Graeme, 2007).

2.2.3.2 - Sustainable flux

Critical flux has been used to describe the relationship between flux and fouling rate in controlled steady state environments (Bacchin *et al.*, 2006). The critical flux means that below this value no fouling occurs and above this level, fouling occurs, the degree of which is a function of flux.

Therefore, it is necessary to develop different tools to understand, predict and control membrane fouling. A practical tool for providing design guidelines for commercial plants is the concept of sustainable flux (Pearce *et al.,* 2007). Sustainable flux is the flow at which a modest degree of fouling occurs, providing an acceptable compromise between high fluxes and restricting the fouling rate (Pearce, 2007). This value depends on the feed characteristics, membrane characteristics, process design and operational designs like the chemical cleaning.

The value depends on feed characteristics, membrane characteristics, process design, and operational requirements (e.g. the cleaning frequency). Pilot trials can be used to establish the relationship between flux and fouling rate for a particular set of circumstances, and evaluate a sustainable flux for a commercially competitive design and operation. Fouling rates increase exponentially with flux (Pearce *et al.* (2007) and Berubier (2007)), so the optimum flux is quite sharply defined for a given membrane and process design.

Considering fouling behavior and the acceptable cleaning frequency, membrane permeability guidelines can be produced for the designer and operator for any system to provide reliable control instructions for stable long term performance.

2.2.4 - Difference with Conventional Activated sludge process (CAS)

As the MBR technology is composed of a biological process with membrane separation stage, the secondary clarifier is not necessary for the solid-liquid separation (Figure 2.4), which means a smaller foot print compared to the CAS (Judd, 2006). Due to the higher MLSS content and higher sludge retention time (SRT) that can be achieved in an MBR compared to a CAS system (table 2.1), results in less secondary sludge production (Metcalf & Eddy ,2003).

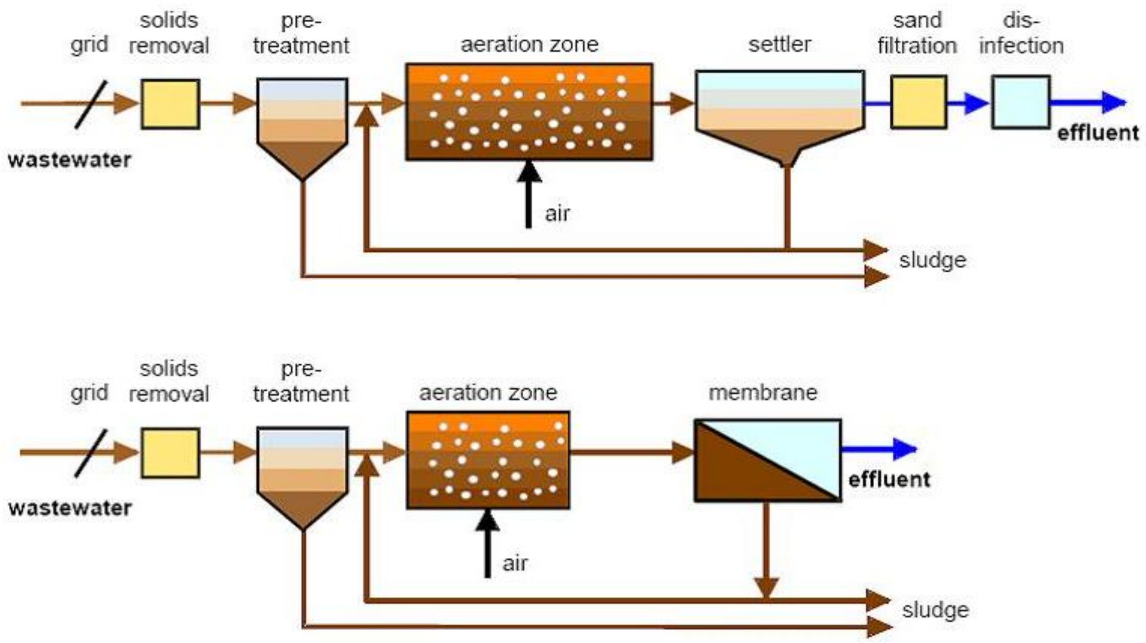

Figure 2.4 - Schematic view of a conventional activated sludge process and of a membrane bioreactor process (Drew, 2008)

Because of their modularity, MBR plants can be scaled-up and resized rapidly, adapting to changes in water flow, load concentrations and temperature variations. With a shorter star-up period produce a reasonably consistent quality of treated water. So MBR plants have more “flexibility” to adaptation of different characteristics of wastewater influent than the CAS. This fact is of great importance in tourist areas *(Ravazzini, 2008)* and, for WWTP upgrades for instances.

The efficiency of nutrients removal and process conditions in MBRs, compared to conventional activated sludge process (CASP) for municipal wastewater treatment are represented in Table 2.1.

However in terms of cost, MBR needs more costs for the membranes, for operation and maintenance than the CAS.

Table 2.1 - Nutrients removal and process conditions in MBRs and conventional activated sludge process (CASP) for Municipal Wastewater Treatment (Kraume et al., 2005).

	Unit	Conventional ASP[a,b,c]	MBR[b]	MBR[c]
SRT	d	10-25	<30	30
HRT	h	4-8[d]	>6	8[d]
MLSS	Kg/m^3	5	12-16	
BOD_5 loading rate	$Kg/(m^3 d)$	0.25 0.32-0.64 [d]		0.4-0.7
BOD_5 (F/M)	Kg/(kg d)	0.05	<0.08	
BOD_5 removal	%	85-95 [d]		98-99
effluent conc.	mg/L	15		
COD removal	%	94.5		99
effluent conc.	mg/L		<30	
TSS removal	%	60.9		99.9
TSS	mg/L	10-15		
turbidity	NTU			
N_{total} removal	%			
effluent conc.	mg/L	<13	<13	
NH_4^+ removal	%	98.9		99.2
P_{total} removal	%	88.5		96.6
Effluent conc.	mg/L	0.8-1	<0.3	

[a] Mudrack, J., *et al.*, 1985, [b] Cui, F., *et al.*, 2003, [c] Cicek, N., *et al.*, 1999, [d] Gander, M., *et al.*, 2000

2.2.5 Advantages/ Disadvantages

Membrane bioreactors (MBR) are composed of a biological process and a membrane separation step.

The process has many advantages:

- excellent and stable effluent quality, including disinfection
- high volumetric load resulting in compact designs and low excess sludge production
- high potential for water reuse

However, due to the membrane separation stage some drawbacks arise:

- high investment and operational costs compared to conventional activated sludge process due to the membrane costs and the need of qualified operators
- membrane fouling resulting in:
    - more extensive pre-treatment required
    - high energy input required to maintain turbulent conditions near the immersed membranes (aeration)
    - regular chemical cleanings

In the MBR process the membrane acts as a physical barrier. Therefore few chemicals are required except for membrane maintenance cleaning. So it completely removes particles, without chemical addition, therefore avoiding chemical contamination of the rejected sludge or treated water (Ravazzini, M., 2008).

2.2.6 - Different technologies available

As was already mentioned in section 2.2.2, the membranes can be incorporated in the process in two different configurations (Figure 2.2):

Immersed membranes in the bioreactor – the membranes are located inside the bioreactor with direct feed inlet (activated sludge) and connections for the outlet (recirculation and permeate). Permeate is extracted by ways of under-pressure and supply of compressed air bubbles from the bottom serves to avoid solids deposition and for oxygenation of the biomass (Metcalf & Eddy, 2003). External (side-stream) - membranes are located outside the bioreactor and the sludge is recirculated through the tubular membranes elements. In the bioreactor a system of air diffusers fed by compressors serves for oxygen supply and sludge homogenization. The permeation takes place inside-out (Metcalf & Eddy, 2003*)*.

Three configurations are available In MBR technology: flat sheet, hollow-fiber and (multi)tubular (Figure 2. 5).

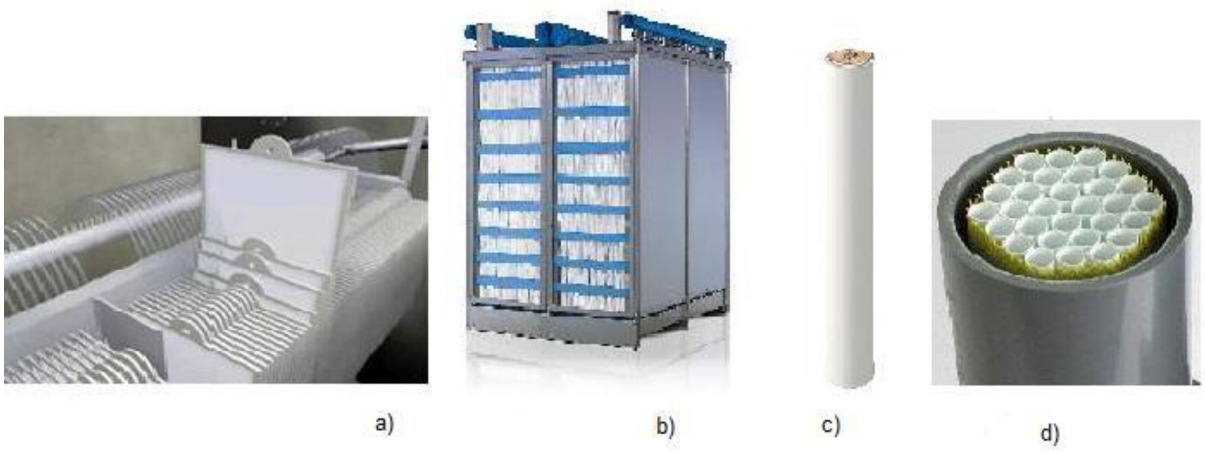

Figure 2.5 - Membrane configurations- a) flat sheet membrane (Copa MBR Technology®), b) Hollow fiber membrane module (KOCH®), c) Hollow fiber membrane (KOCH®), d) (multi) tubular membrane (INDUCOR®)

Each one is utilized depending on the application as it is possible to see in Table 2.2. The feed operation performance for each configuration is: outside-to-in for flat sheet, inside- to-outside for multi-tubular and for hollow-fiber both modes of operation are possible.

Table 2.2 - Membrane configurations and respectively cost and application (Judd, 2006)

Configuration	Cost	Application
Flat sheet	High	UF, RO
Multi-tubular	Very high	MF, UF, NF
Hollow-fiber	Very low	MF, UF, NF, RO (inside out)

Membranes offer the possibility to choose different types of filtration selectivity depending on the membrane pore size. The coarsest membrane is microfiltration (MF), with a pore size around 0.1-1 µm, it is capable to remove particulate matter. Next is ultrafiltration (UF) which its pore size range is around 0.01-0.1 µm and it removes mostly viruses and colloids. Than is the nanofiltration (NF) with a pore size range around 0.001-0.01 µm, it removes small molecules and viruses. The most selective membrane, associated with reverse osmosis (RO) with a pore size range around 0.0001 – 0.001 µm, it removes all the dissolved substances (Judd, 2006). So it is possible to choose the most adequate membrane, depending on which type of constituents on wastewater it is necessary to remove.

3 – METHODOLOGY

3.1 - Delft Filtration Characterization method

The Delft filtration characterization method (Dfcm) was used to analyze the filterability of the activated sludge samples and the influence of different cross-flow velocities on sludge filterability. This method was a key tool for the development of this research. The Delft Filtration Characterization installation (DFCi) was developed by Delft University of Technology (TU Delft). It has a singular tubular Polyvinylidene difluoride (PVDF) membrane module, provided by X-flow, approximately with 1m length, operated in cross-flow mode, with diameter of 8mm and nominal pore size 0.03µm, therefore considered UF (Dfcm protocol is referred in Appendix I). Samples of 20l of activated sludge are circulated with a peristaltic pump (Figure 3.1) and permeate is also extracted with a peristaltic pump and permeate mass balance (Figure 3.2).

Figure 3.1 - Sludge peristaltic pump

Figure 3.2 - Permeate peristaltic pump and permeate mass balance

The installation has sensors, for monitoring the trans-membrane pressure (TMP), cross-flow velocities, temperature, dissolved oxygen concentration, pH and with a laptop connected to a mass balance, the permeate flux is measured. Demi-water (distilled water) is used for the membrane cleaning. The scheme of the installation is presented in Figure 3.3 followed by a picture of the installation, Figure 3.4. The unit is specifically described in Evenblij *et al.* (2005). The operation with different flows is possible due to a PLC (programmable logic controller) (Figure 3.5) that switches pumps on and off and also opens or closes valves.

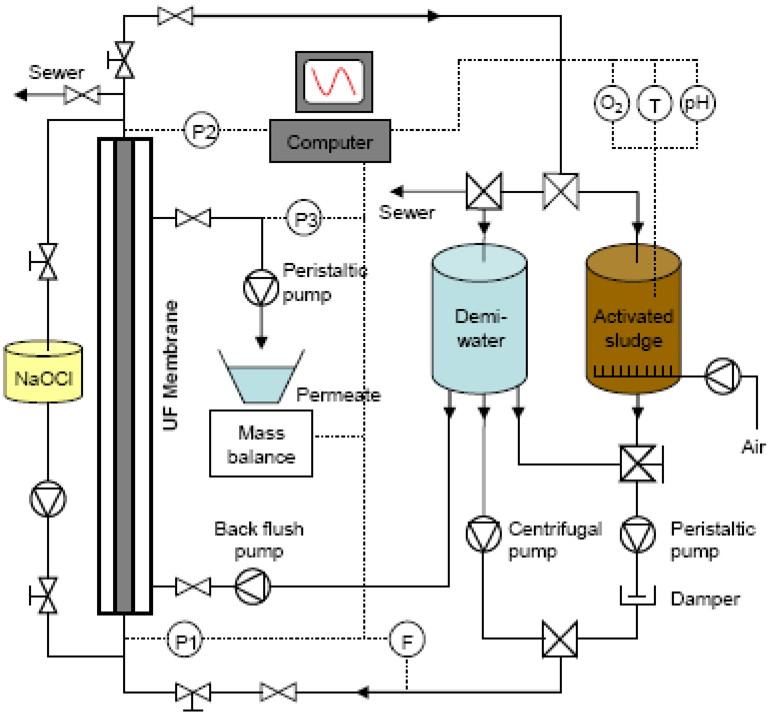

Figure 3.3 - Delft Filtration Characterization installation (Dfci) scheme (Evenblij et al., 2005)

Dfci legend

(P)	pressure sensors		three way valve, operated via PLC
(F)	flow meter		three way valve
	two way valve, operated via PLC		two way valve, manually operated

Figure 3.4 - Picture of Dfci

Figure 3.5 - PLC, programmable logic controller

One filtration cycle is completed after achieving 20 L/m^2 of permeate extraction, a TMP value of 0.5 Bar or permeate mass extracted of 500 g. This usually takes fifteen minutes. After filtration of 20 L/m^2 of permeate, using a flux of 80 L/(m^{2}h) and a cross-flow velocity of 1 m/s (standard conditions) an additional resistance (ΔR20) is registered, than the information will be gathered in a single data file for consequent treatment on Microsoft Office Excel. This permits that all sludge samples are filtered and compared under identical hydraulic circumstances. The standard conditions are utilized to make possible the comparison of different research projects with Dfci, on TU Delft.

3.1.1 - Additional resistance (ΔR20)

The ΔR20 (*10^{12}/m) is the parameter used to characterize the filterability of the sludge sample; it is the activated sludge sample tendency to originate fouling. It is defined as the increase in resistance after a specific permeate production of 20 L m^{-2}. The additional resistance of an activated sludge sample is the difference between the activated sludge sample membrane resistance and the clean membrane resistance.

The sludge samples were collected by the recirculation pipe at the end of the filtration cycle. After a cycle, when ΔR20 values are lower than 0.2 the sludge is considered to have a good filterability, higher than 1 indicate bad filterability and between 0.2 and 1 is considered average filterability. In this thesis for the cross-flow velocities below 0.7 m/s are considered low, between 0.7m/s and 1m/s it is average velocity and above 1m/s is high velocity.

The sludge samples, filtrated straight after gathering from WWTP, are representative for the sludge filtration performance in the full scale MBR.

3.2 - Heenvliet wastewater treatment plant

In response to water management problems due to the lack of adequate laws, the European Union responds with a policy development related to water management. It was implemented the European Water Framework Directive which became effective in 2006. This created new laws in urban wastewater like defining new nutrients limits in water discharges, for example the Maximum tolerable risk (MTR) (Uijterlinde *et al.*, 2005).

To achieve part of the targets established by the European Union, the Netherlands chose the relatively new MBR technology for its compactness. They started developing research programs and studies to test MBR pilots for Wastewater Treatment Plant upgrade (Uijterlinde *et al.*, 2005).

One of the chosen was Heenvliet WWTP, where the treatment must achieve the effluent requirements and targets presented in Table 3.1.

Table 3.1 - Effluent requirements and targets (Bentem et al., 2005)

Parameter	unit	Required		Target	
Year	-	2006		2010	
Season	-	summer	Winter	Summer	Winter
BOD_5	mg/L	-		-	
NH_4-N	mg/L	1	-	1	-
N_{total}	mg/L	5		2.2	
P_{total}	mg/L	0.3		0.15	
SS	mg/L	-		-	
E-coli	-/mL	20		20	

This WWTP located thirty five kilometers from TU Delft, receives 8,950 population equivalents (p.e.) of domestic wastewater. The hydraulic capacity will increase to 390m^3/h when the Abbenbroek WWTP (capacity 1,650p.e.) will be connected to Heenvliet WWTP. It is operated as a low-loaded activated sludge system; type carrousel and MBR, with one secondary clarifier and disinfection of the effluent with sodium hypochlorite before being discharged to local surface water which is used for public leisure (Mulder *et al.*, 2005), more specifications of the WWTP are described in Table 3.2.

Table 3.2 - Specifications of the plant (Mulder et al., 2005)

	Units	Conventional	MBR
Screens	mm	6 (bars)	3 (pores)
Maximum Hydraulic load	m^3/h	290	100
Biological capacity	p.e.(136grBOD/p.e./day)	9,660	3,330
F/M ratio	gBOD/gMLSS*d	0.045	0.045
Sludge concentration	$kgMLSS/m^3$	4.7	10
Surface load clarifier	m^3/m^2*h	0.51	-
Net membrane flux	L/m^2*h(at $100m^3/h$)	-	24.3
Maximum possible flux	L/m^2*h	-	56.3
Disinfection	-	NaOCl	Ultrafiltration

It is possible to visualize a scheme and a panoramic picture of Heenvliet WWTP in Figure 3.6 and Figure 3.7.

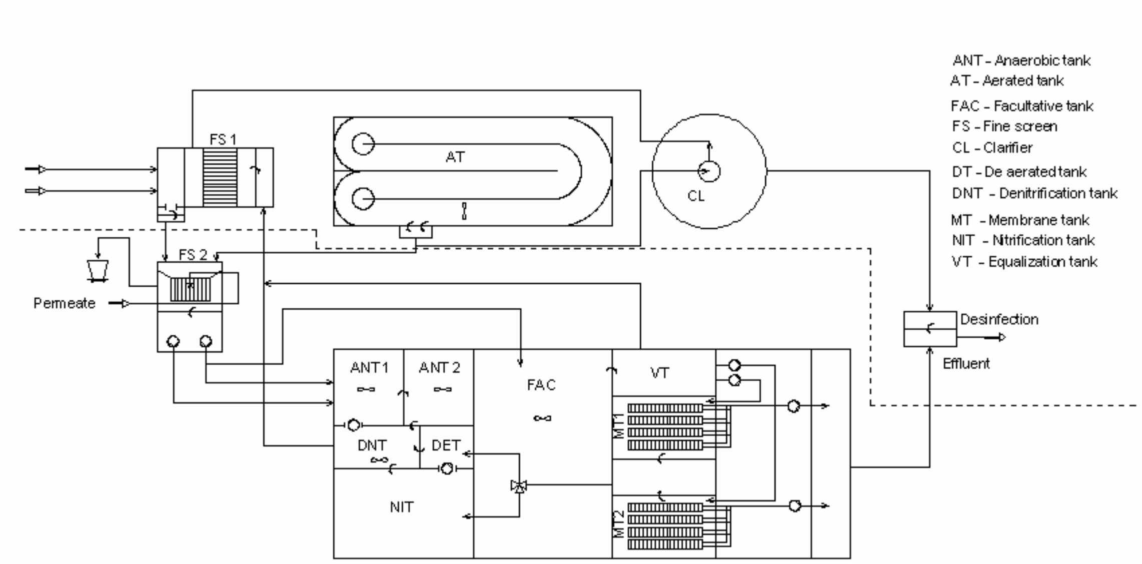

Figure 3.6 - Flow sheet of Heenvliet WWTP

Figure 3.7 - Panoramic picture of Heenvliet (Photo: Aerofoto Brower- Brummer)

The MBR module was installed early 2006, it was designed to treat 100m^3/h. This represents the dry weather flow (25% of the total hydraulic load). Two parallel membrane tanks (Figure 3.8) are equipped with Toray flat sheet UF membranes, with nominal pore size 0.08µm, with the pumps for activated sludge circulation and permeate extraction for constant flux filtrations (see Figures 3.9, and Figure 3.10, respectively).

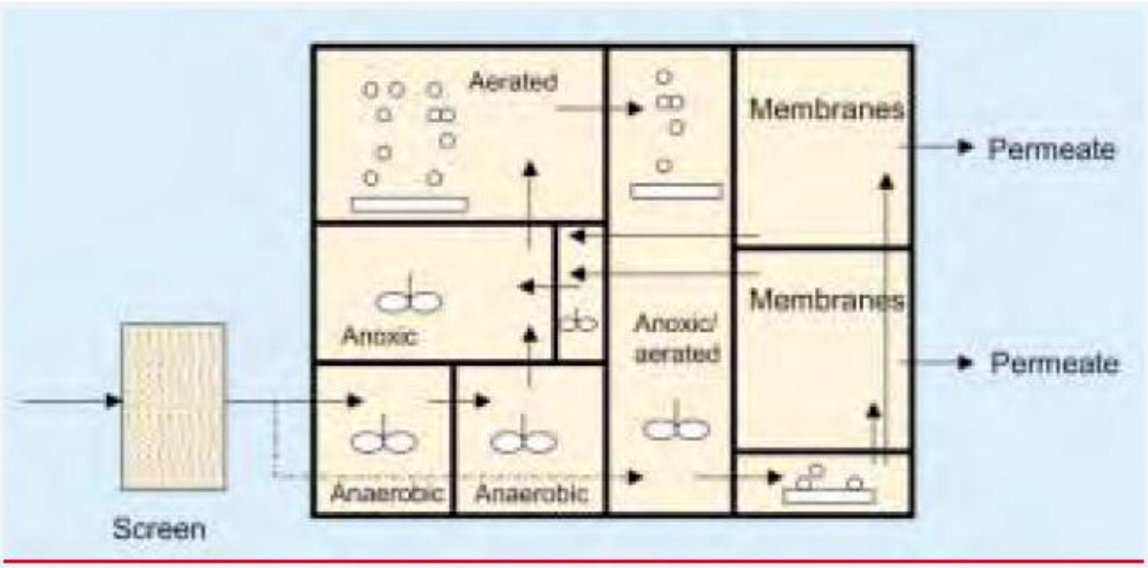

Figure 3.8 - Flow sheet of the MBR (Mulder et al., 2005)

Figure 3.9 - Activated sludge pumps

Figure 3.10 - Permeate extraction pumps

This new system is called a Hybrid since it combines the advantages of MBR (high effluent quality, space savings) with the advantages of conventional activated sludge plants which can process large volumes of wet weather discharges (Mulder *et al.*, 2005).

At first the two treatment processes were operating in series. The MBR received the wastewater after it passed through the carrousel. The result of this was biological system able to separate sludge from water by both membrane filtration and sedimentation. The secondary clarifier was used only when the total flow exceeded the MBR capacity. Then after the 2nd of March of 2009 the treatment process was changed to parallel and the hydraulic load was distributed at 75% for the CAS and 25% for the MBR (Figure 3.11).

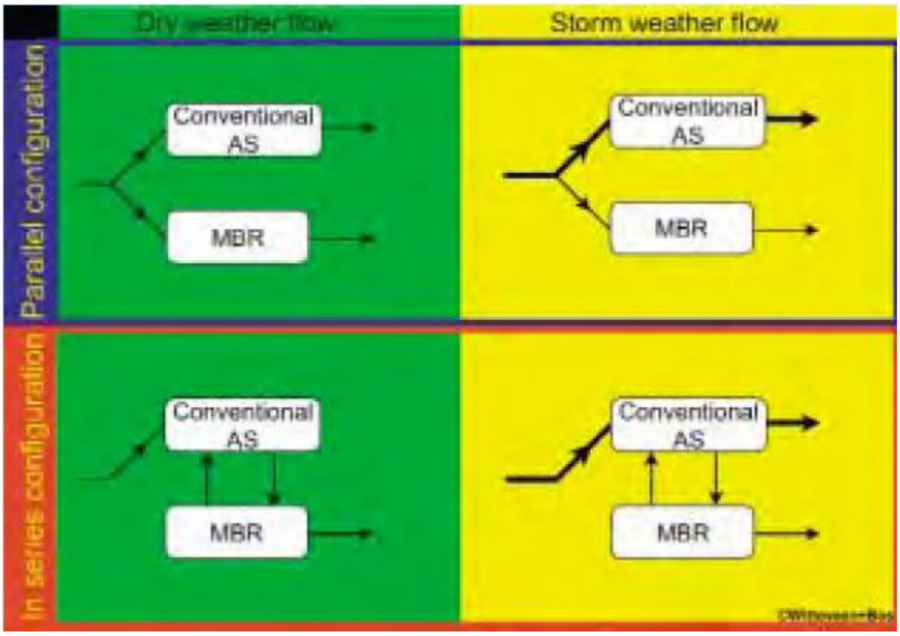

Figure 3.11 - Possible configurations of the hybrid system during dry weather flow and storm weather flow. (Mulder et al., 2005)

For the future there are some challenges to be overcome in Heenvliet WWTP, like decreasing the energy consumption trough the possibility of using only one instead of two membrane tanks working at the same time. Another goal is to optimize the treatment process to achieve the MTR of nitrate and phosphorous in the discharges water.

3.3 - Parameters used for research

Right after Dfci was used to analyze the filterability of the activated sludge samples, the influence of different cross-flow velocities on sludge characteristics, was identified using five analyses: the total suspended solids (TSS) and volatile suspended solids (VSS) (mixed liquor suspended solids, materials and methods are referred in appendix II), chemical oxygen demand (COD materials and method referred in appendix III), total organic demand (TOC materials and method referred in appendix IV) and Particles counting in range 0.4 – 0.5µm (materials and method referred in appendix V). The aim of these five analyses was to fractionate the sludge samples, into the three considered compounds which influence membrane fouling, suspended solids, colloids and solutes (Le-Clech *et al.*, 2006). For this thesis suspended solids were associated to the TSS and VSS analyses, the colloids to the COD and particles counting and the solutes to the TOC analyses.

4 – RESULTS AND DISCUSSION

4.1 - Experimental protocol

The experimental protocol in this thesis consists of several sets of experiments. The analyses were performed almost weekly from 24th of February to 15th of June, with a break in proceedings during May. The first three days of a week were used for the laboratory analysis and the other two days were used for data processing using MS Excel.

On the first day 30 liters of sludge samples for analyses were collected from the MBR tank at Heenvliet WWTP (Figure 4.1).

Figure 4.1 - Membrane tank sludge collection process

Back to TU Delft water lab, the sludge samples were placed in the sludge source device of the Dfci equipped with an oxygen aeration system for the supply of atmospheric oxygen with air bubbles. After 30 minutes (for adaptation of the sludge biomass to the new conditions), two standard filtrations (CFV 1.0 m/s) were performed. Right after the last filtration half a liter of sludge was extracted from the recirculation pipe of the Dfci to carry out the TSS, VSS, COD, TOC and particles counting analyses. On the next two days of analyses the same procedure was executed (using the same sludge samples), but with different cross-flow velocities, below or above 1 m/s, for each day.

4.2 - Heenvliet WWTP site Monitoring

While the different cross-flow filtrations analyses were made, an on-line monitoring of Heenvliet full scale plant was carried out, with the standard filtration analyses (Cross-flow velocity 1m/s, flux of $80L/m^2h$).

The additional resistance values acquired with the Dfci were related to the sludge temperature, the COD values, number of particles counting in the diameter range of 0.4 – 5 µm, TSS and VSS, measured in Heenvliet WWTP.

At Heenvliet WWTP, the treatment process was in series until the 2nd of March, the MBR received wastewater after it passed through the carrousel. After that date the treatment process was changed to parallel and the hydraulic load was distributed on 75% for the CAS and 25% for the MBR.

In the first configuration with the process in series a biological system was created capable of separating sludge from water by both membrane filtration and sedimentation. When the process changed to parallel, the MBR was receiving sludge with higher organic load. This caused a decrease in efficiency until the balance in the food to microorganism (F/M) ratio, was achieved, with increasing the ΔR20 and the maximum COD value. This situation is represented in Figure 4.2 showing the higher values of both parameters (ΔR20 and COD) on 4-3-2009 at 11:00. Like Bouhabila *et al.* (2001) mentioned, the F/M ratio it is relative to the COD measurements (Bouhabila *et al.,* 2001) and so the filterability.

The deviations in COD values could be associated with significant variations in the raw inflow wastewater concentrations (Figure 4.2).

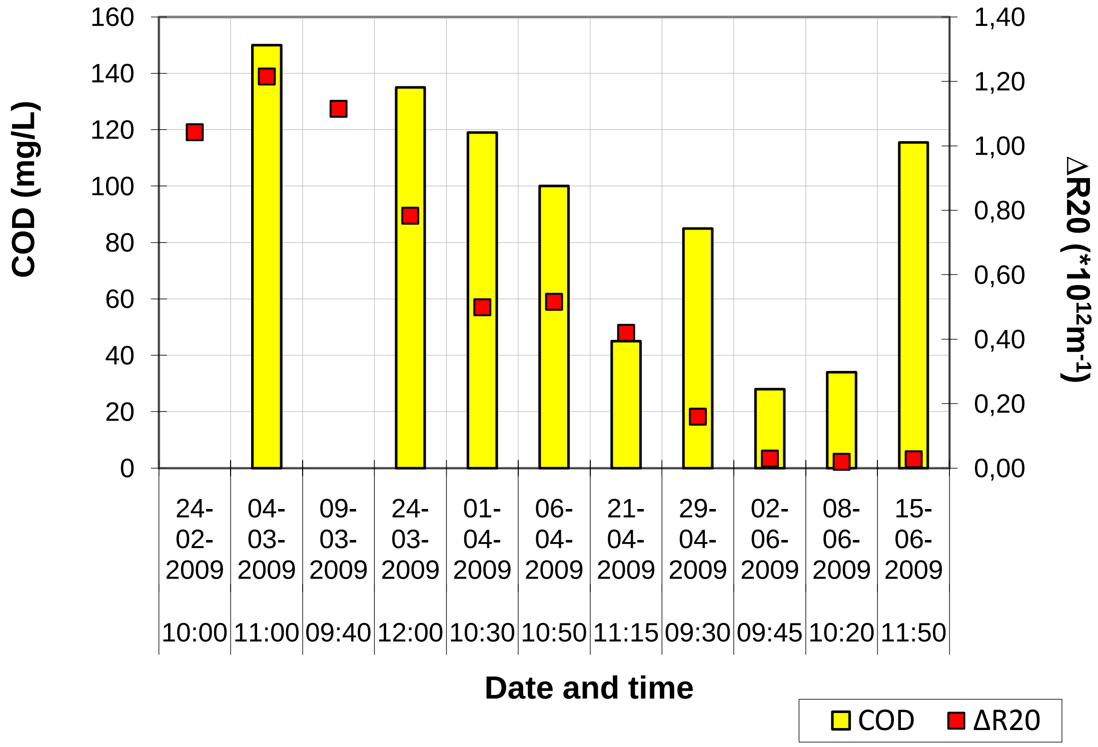

Figure 4.2 - Development of the additional resistance and the chemical oxygen demand

The membrane resistance was decreasing as the MBR process adapted and stabilized to the new treatment conditions. At the beginning of April it was possible to identify the process stabilization, as shown on the chart of Figure 4.3.

Afterwards the process became more efficient as the filterability improved. One of the associated reasons is the increasing temperature, as a consequence of the seasonal variations (Figure 4.3).

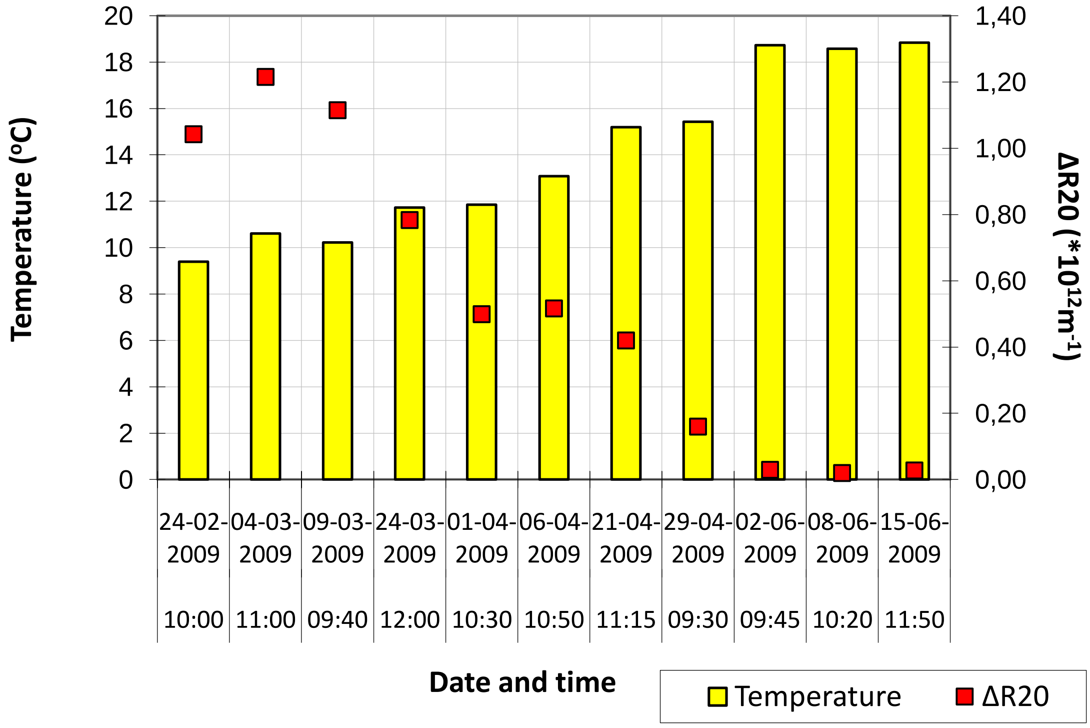

Figure 4.3 - Evolution of the additional resistance and the temperature

As for the analyses referring to the number of counted particles in the diameter range of 0.4 – 5 µm it is possible to identify a strong correlation (R^2 value is approximated to 1) between the deterioration of the filterability and the release of particles in the permeate (Figure 4.4).

As the ΔR20 increases the number of particles in the concentrate (free water) also increases (Figure 4.4). The additional increase in resistance could be associated to the higher deposition of particles at the membrane surface, increasing the membrane permeability mentioned by Petsev *et al.* (1993) referred by Le-Clech *et al.* (2006) mentioned an increase of the additional resistance of the membrane, so the particles will continue on the concentrate.

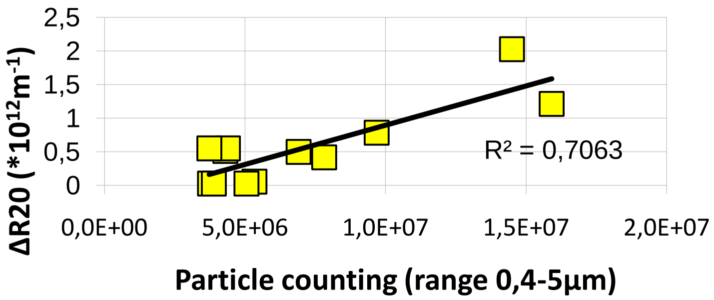

Figure 4.4 - Number of particles counting (diameter range 0.4– 5µm) distribution and respectively additional resistance

No correlations could be demonstrated between filterability TSS and VSS in this study as is shown in the Figure 4.5 and Figure 4.6. The TSS and VSS values do not vary very much as the sludge filterability is reduced. Therefore these values are not relevant for this study.

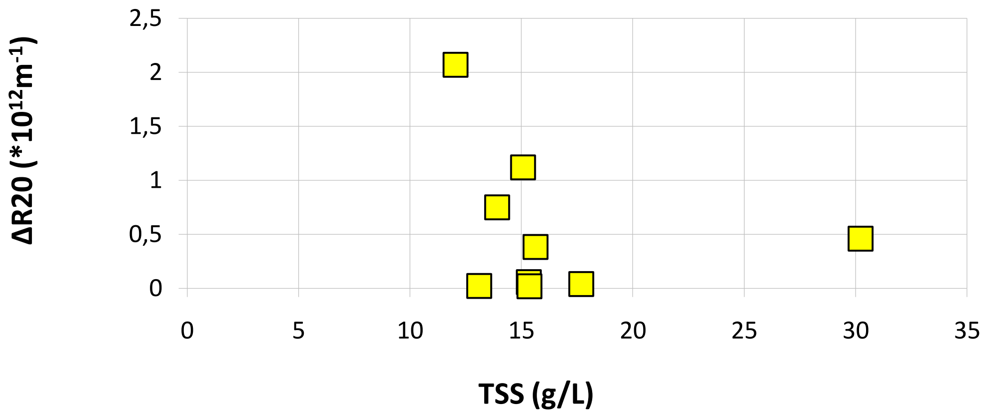

Figure 4.5 - Relation between TSS and VSS values for each additional resistance sludge sample

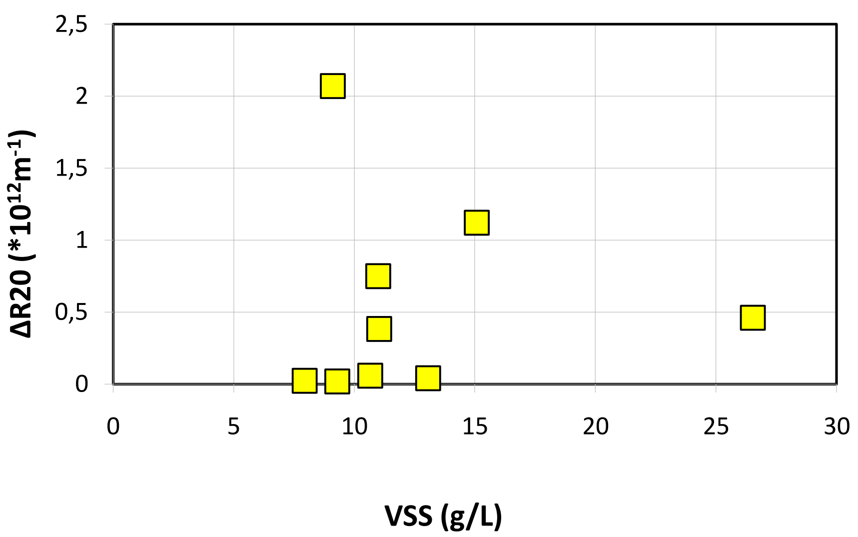

Figure 4.6 - Relation between TSS and VSS values for each additional resistance sludge sample

4.3 - The influence of different cross-flow velocities on the filterability of different types of activated sludge

The quality of the different types of sludge samples were distinguished as good bad and average, considering the filterability. If ΔR20 was lower than $0.2*10^{12}m^{-1}$ the sludge was good, higher than $1*10^{12}m^{-1}$ indicate bad sludge and between $0.2*10^{12}m^{-1}$ and $1*10^{12}m^{-1}$ is considered average quality sludge. The same for different ranges of cross-flow velocities like: low velocity below 0.7 m/s, between 0.7m/s and 1m/s it is considered average velocity and above 1m/s is high velocity. The influence of different cross-flow velocities in the sludge filterability was analyzed taking into consideration the obtained data for each parameter (COD, TOC and particles counting).

4.3.1 - Particles counting in the diameter range of 0.4 – 5 µm

Particles are always present in all types of water. By measuring them it is possible to define treatment plant influent, designing treatment processes, change operations and determining efficiency (Metcalf & Eddy, 2003).

Before the particles counting the wastewater sample is filtrated, with vacuum filtration and a Whatman® 589/2 Round filter paper with 7-12μm pore size to originate free water (supernatant). The numbers of particles counts are plotted against filterability data for each type of sludge with their respective cross-flow velocity in Figure 4.7.

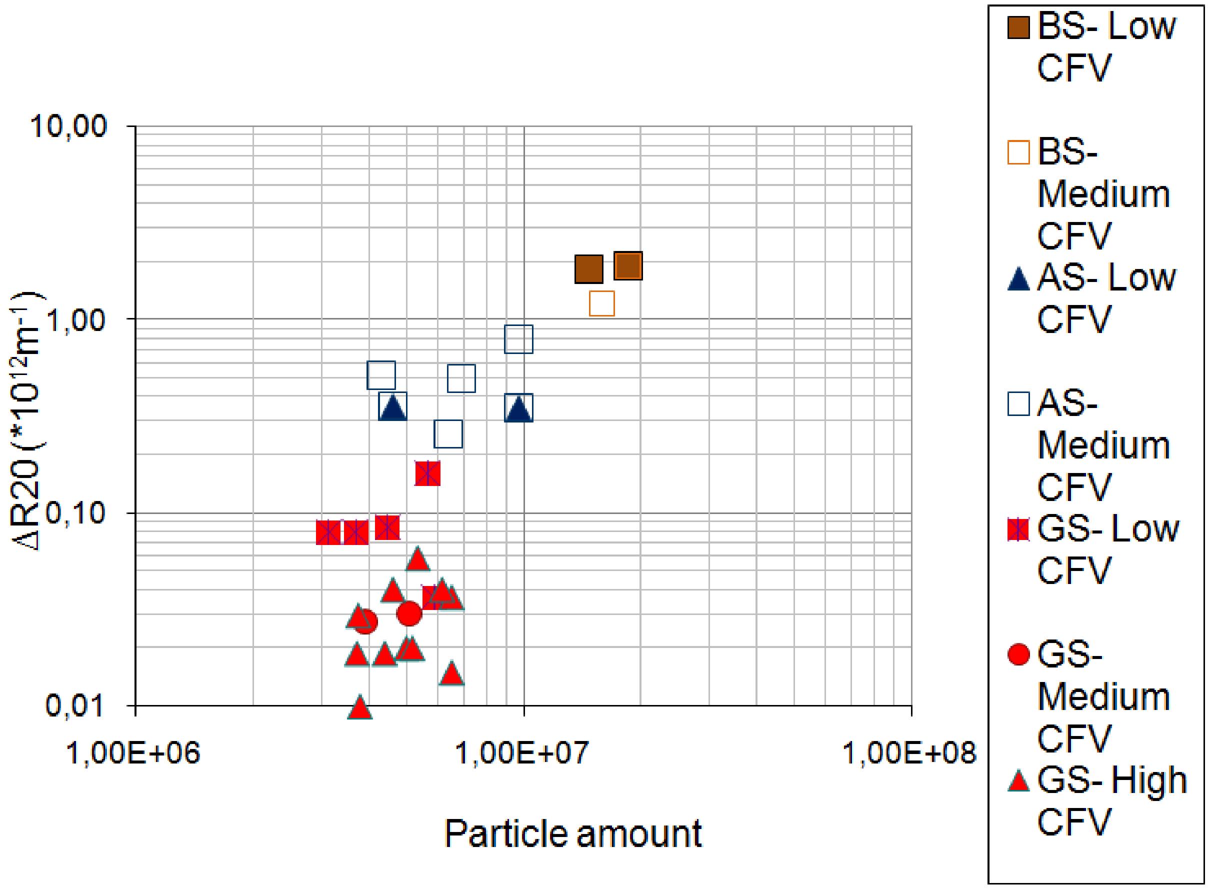

Figure 4.7 - Particles counting (diameter range 0.4 – 5μm) distribution and respectively additional resistance, for each type of sludge and specific cross-flow velocity.

As can be observed the distribution of values does not show a clear trend between these parameters (Figure 4.7). Even if the trend is not clear, differences are still noticeable: it is possible to detect that bad sludge contains bigger amount of particle then the average sludge, still bigger amount of particle than the good sludge. Also average sludge seems to contain more particles then the good sludge.

4.3.2 - Chemical Oxygen Demand (COD)

COD tests were used to measure the oxygen equivalent of the organic material in wastewater (Metcalf & Eddy, 2003). Most applications of COD determine the amount of organic pollutants found in water (Clesceri *et al.*, 1998). It is expressed in milligrams per liter (mg/L), which indicates the amount of oxygen consumed per liter of solution.

The COD values are plotted against filterability data for each type of sludge with the respective cross-flow velocity in Figure 4.8, to identify correlations between the parameters. But, as can be observe the distribution of values does not show a suitable trend between these parameters. However COD seems to influence the ΔR20, as the COD increases the ΔR20 increases.

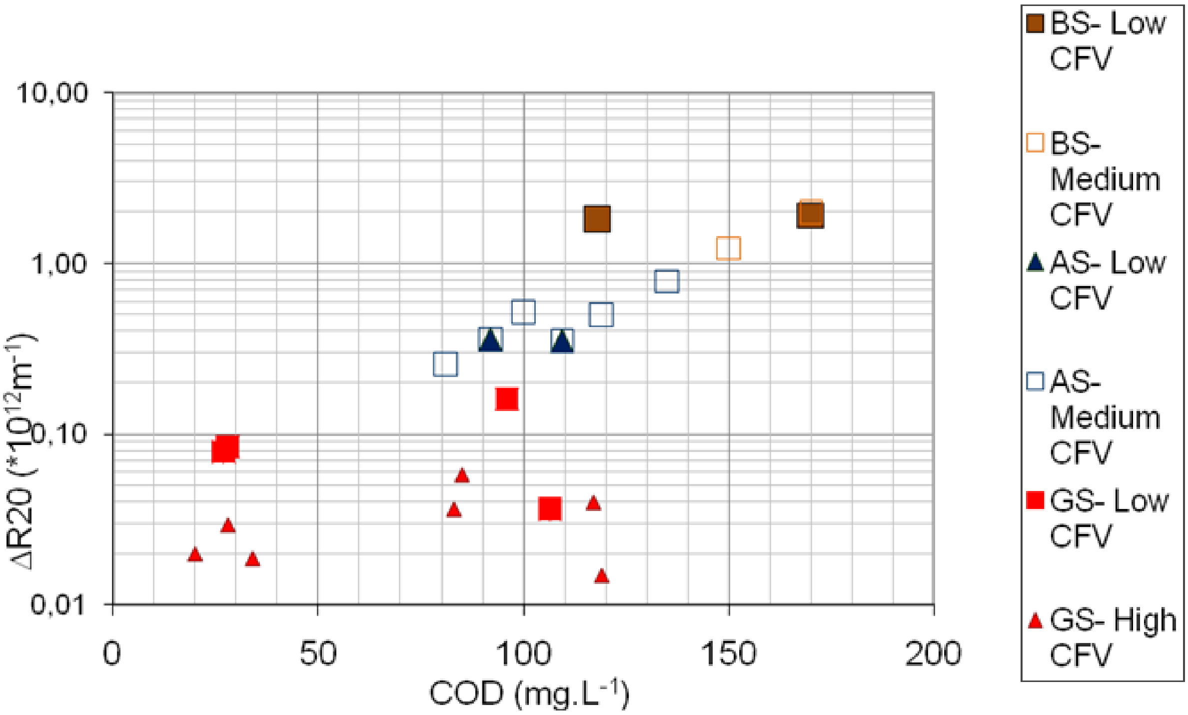

Figure 4.8 - Chemical organic demand and respectively additional resistance, for each type of sludge and specific cross-flow velocity.

4.3.3 - Total Organic Carbon (TOC)

TOC tests were used to measure the total organic carbon in an aqueous sample *(Clesceri et al., 1998)*. The TOC in wastewater can be used as a measure of its pollution characteristics. The TOC can be fractionated in order to get information about the different fractions present in the sample (colloids and soluble) (Metcalf & Eddy, 2003). Before measuring TOC the wastewater sample is filtrated, with vacuum filtration and a Whatman® 589/2 Round filter paper with 7-12µm pore size to obtain free water. For the soluble material that passes through both filter steps to classified as dissolved, the free water sample must be fractionated using a VWR 25 mm syringe and a filter with pore size 0.45µm (Tao, S. (1996)) (Figure 4.9).

Figure 4.9 - Syringe and a filter with a pore size 0.45µm

The TOC values are plotted against filterability data for each type of sludge with the respective cross-flow velocity in Figure 4.10. But, as it is possible to observe the distribution of values does not show relationship between the parameters. However TOC seems to influence the ΔR20: as the TOC increases the ΔR20 also increases.

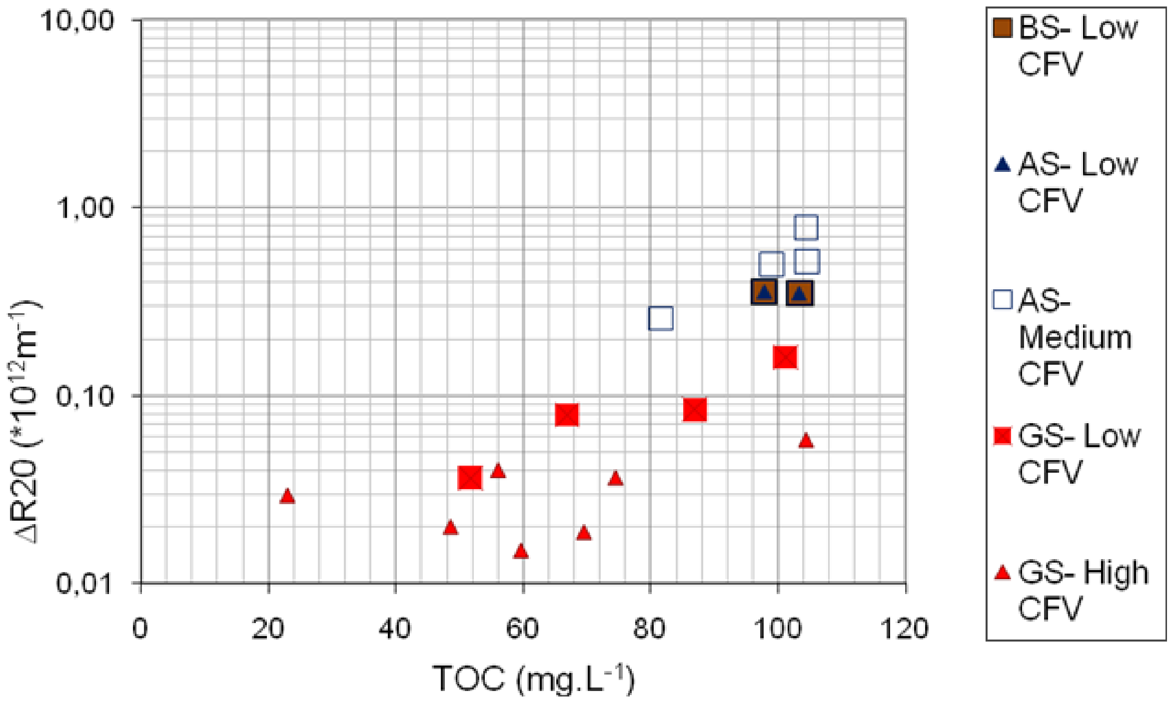

Figure 4.10 - Total organic carbon and respectively additional resistance, for each type of sludge and specific cross-flow velocity

4.4 - The influence of different cross-flow velocities on the filterability of activated sludge.

The way the acquired data were plotted does not give good answers for the objective of this thesis. Therefore the types of sludge were grouped. So the new plots were done with the three analyzed parameters versus the three initially defined cross-flow velocities.

4.4.1 - Particles counting in the diameter range of 0.4 – 5 µm VS ΔR20

The following plot shows the influence of particles in the diameter range of 0.4-5µm. on the filterability of the sludge with the three initially predefined cross-flow- velocities.

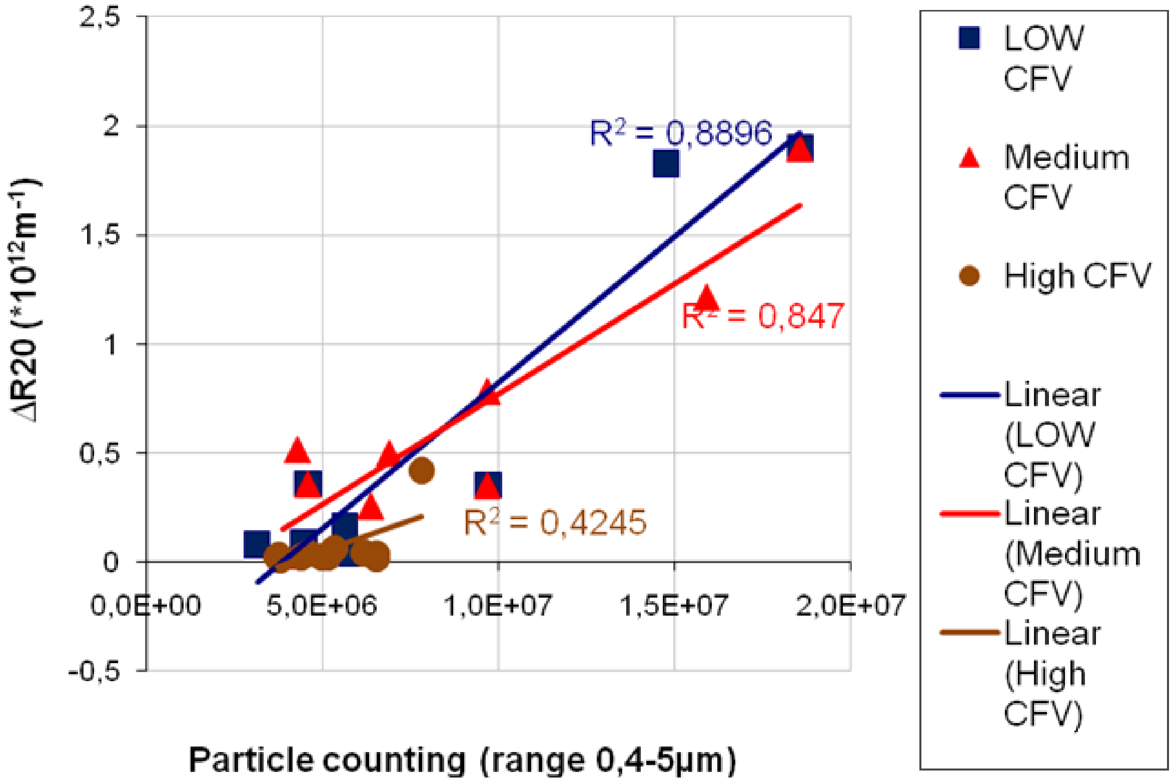

Figure 4.11 - Particles counting (diameter range 0.4 – 5µm) distribution and respectively additional resistance, for each cross-flow velocity

Figure 4.11 shows:

- Strong correlation between the additional resistance and number of counted particles (diameter range 0.4 - 5µm) for Low and Medium CFV. This means that an increasing in the number of counted particles (diameter range 0.4 - 5µm) reflects the increase of ΔR20.

-Weak correlation between the additional resistance and number of counted particles (diameter range 0.4- 5µm) for High CFV.

4.4.2 - Chemical Oxygen Demand (COD) VS ΔR20

Figure 4.12 shows the influence of COD on filterability of the sludge with the three initially predefined cross-flow- velocities, where can be seen:

- Strong correlation between the additional resistance and COD for Medium CFV and Low CFV. Which means the increase in COD reflects the increase of ΔR20.

- Weak correlation between filterability and COD for High CFV

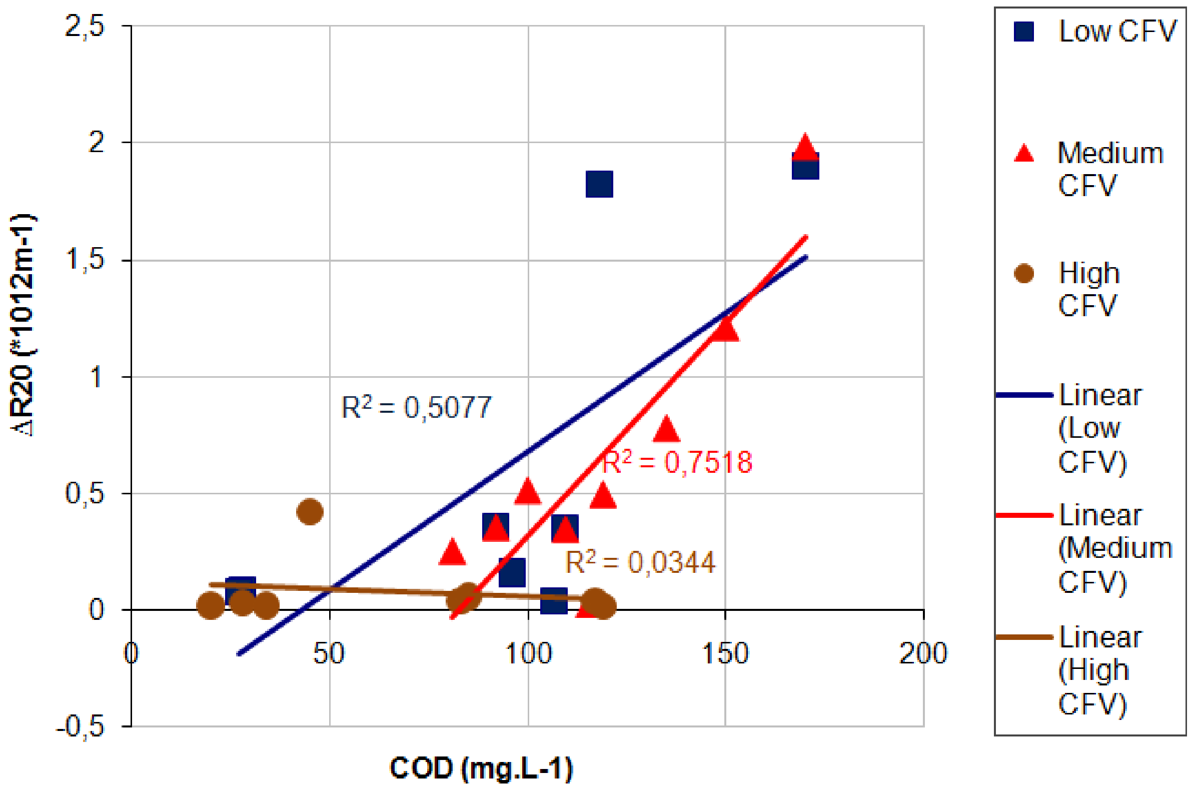

Figure 4.12 - Chemical oxygen demand and respectively additional resistance, for each specific cross-flow velocity.

4.4.3 - Total Organic Carbone (TOC) VS ΔR20

The following plot shows the influence of TOC. In the sludge filterability with the three initially predefined cross-flow- velocities.

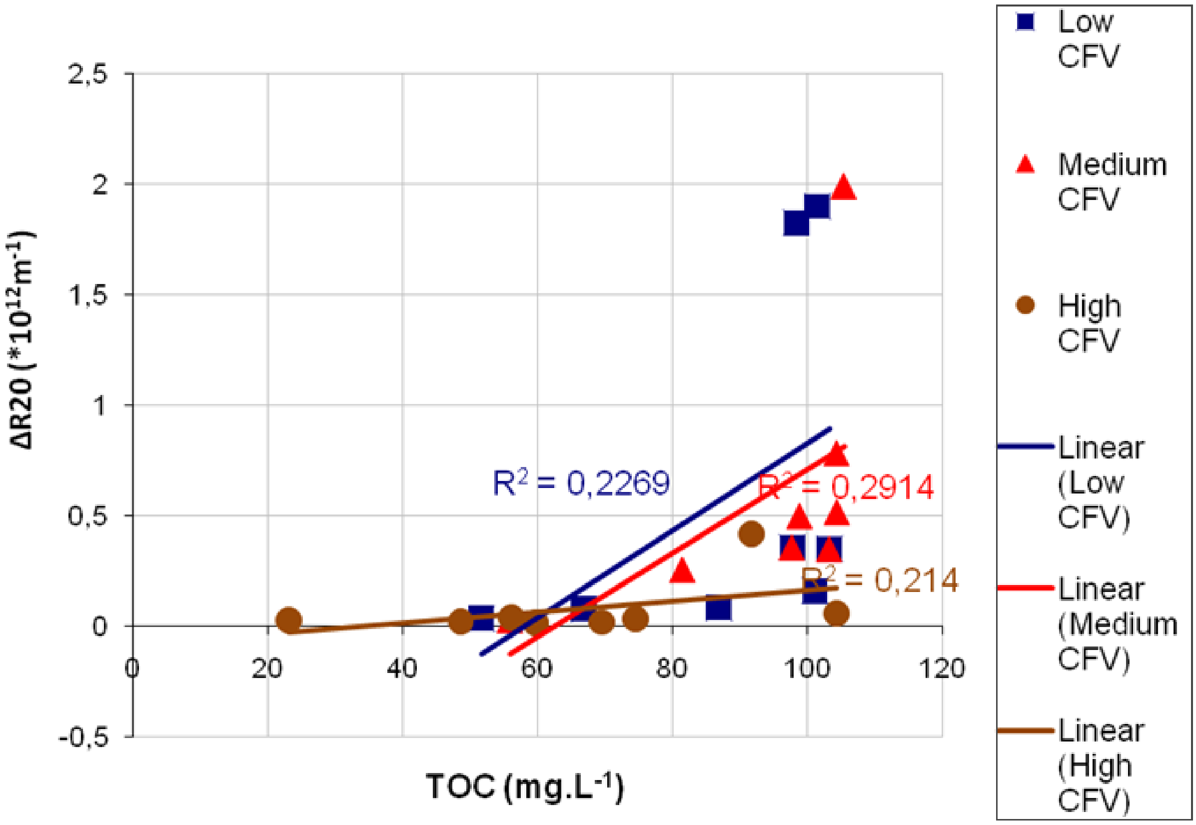

Figure 4.13 - Total organic carbon and respectively additional resistance, for each specific cross-flow velocity.

This graphic show:

- Weak correlation between filterability and TOC for the three ranges of cross-flow velocities.

4.4.4 – Physical interpretation of the results

From the overall analysis of the results and their physical interpretation, the following practical relations can be obtained:

- The particles deposition on the membrane for the high CFV in Figure 4.11 could be associated with the fact that high shear forces break the structure of the activated sludge flocs. Therefore free water is release, as Rosenberger *et al. (*2006) mentioned. As colloids and particles are disrupted, they will be dissolved into the soluble fraction, increasing the TOC values and improving filterability for High CFV, as can be seen in Figure 4.13.

- Considering the low CFV and medium CFV, the colloid fractions have strong influences on activated sludge filterability. The shear does not have the same influence as it has for high CFV. For this reason the colloidal fraction influences filterability as can be identify in Figure 4.11 and Figure 4.12.

- The CFV did not show associations between TOC and filterability, as the correlations are very weak (Figure 4.13). The soluble fraction does not influence filterability, contrary to the findings of Rosenberger *et al. (*2002), mentioned by Evenblij *et al.* (2005).

The main reason could be related to the fact that, as the soluble fraction passes through the membrane, the organic compounds might be retained by absorption in the membrane pores. With a biological development this could generate serious problems on the membrane, originating pore blocking. But as the Dfci filtrations only take fifteen minutes then it suffers a cleaning process and after a day of filtrations a chemical cleaning is performed, these types of problems are not possible to analyze.

-In relation to the cross flow velocity influences on tubular membrane fouling, the best values of filterability were the high CFV, which caused less particle and colloids deposition (Figure 4.11 and Figure 4.12). From low and medium CFV data, it is not possible to draw conclusions.

5 – CONCLUSIONS

The two phases in this thesis were monitoring the Heenvliet WWTP, and perform a set of experiments focused on the influence of the cross-flow velocity on tubular membrane fouling.

The number of measurements for this thesis is quite small; therefore conclusions can only be drawn with some reservations. Still it was possible to detect an influence of the CFV on membrane fouling and good correlations on biological treatment stabilization and temperature changes, in Heenvliet WWTP monitoring.

In relation to the first phase, the obtained data showed a good relation between process progress with temperature and COD analyses in the WWTP. The $\Delta R20$ decreases when temperature increases. And the maximum value of COD corresponds to the worst process situation of the Membrane reactor (when the process changed from series to parallel).

The second phase which is related to the experimental analyses focused on the influence of the cross-flow velocity on tubular membrane fouling. The main conclusion is that for high cross-flow velocity (above 1m/s) the membrane is more efficient in the filtration process. Maybe because of the precision in relation to chemical compounds and physical processes, only four months of analyses are not sufficient, to obtain strong results. This could be a reason to the fact that only for high cross-flow velocities the obtain data allow to draw conclusions.

6 – RECOMMENDATION FOR FURTHER RESEARCH

Further research is suggested on the practical procedure. Performing the TOC, COD and particles counting analyses on the supernatant and permeate in order to identify the amount of colloids and soluble fraction retained by the membrane. In other words, to identify the amount of colloids and soluble fraction that is theoretically available for cake layer formation, since it is larger than the membrane pore size.

The lack of time for the research and the limited range of velocities on Dfci activated sludge peristaltic pump, did not permit the identification of the most favourable value of CFV for the best balance between energy consumption and efficiency of the membrane. For a following research identify the maximum value of cross-flow velocity, that membrane efficiency stabilizes. And discover the best value for energy efficiency and effluent quality.

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APPENDIX I- Delft Filtration Characterization Method Protocol

First cleaning

Check valve of the membrane (top, bottom and sides)

Open the 3 way valve of water

On PLC

Sludge	Water	Flush	Recirculate	Backflush
	X	X		OFF

Start water submerged pump (9)

After some time (After se sludge passing out the membrane)

Recirculate on the PLC

Sludge	Water	Flush	Recirculate	Backflush
	X		X	OFF

After 5minutes

Switch off the water submerged pump (9)

Close the 3way valve for water

Set the Plc

Sludge	Water	Flush	Recirculate	Backflush
X		X		OFF

Put the system back to atmospheric pressure (0.00 bar)

Sludge	Water	Flush	Recirculate	Backflush
X		X		ON

Wait until you see water running in the sewage and then back to OFF

Experiment

PLC is

Sludge	Water	Flush	Recirculate	Backflush
X		X		OFF

Check the computer file start (year-month-day)

Start the sludge pump (yellow)

When sludge is coming out

Sludge	Water	Flush	Recirculate	Backflush
X			X	OFF

Check pressure sensor display with computer values

Check flowmeter (1m/s 184L/h)

Check damper (not filling)

After 20L/m of permeate extraction or TMP =0, 5 Bar

Switch of permeate pump (green)

Switch of sludge pump (yellow)

Switch of the software program

Start a cleaning step 1)

Appendix II – Standard Methods for MLSS

In this research the Standard Methods for the examination of water and wastewater (20th Edition) were used for the TSS and VSS analyses (Clesceri *et al.*, 1998).

The MLSS protocol written by Clesceri *et al.* (1998), in Standard Methods for the Examination of Water and Wastewater – 20th Edition and it was mentioned on Piedade (2009).

2540 D. Total Suspended Solids Dried at 103–105°C

1. General Discussion

a. Principle: A well-mixed sample is filtered through a weighed standard glass-fiber filter and the residue retained on the filter is dried to a constant weight at 103 to 105°C. The increase in weight of the filter represents the total suspended solids. If the suspended material clogs the filter and prolongs filtration, it may be necessary to increase the diameter of the filter or decrease the sample volume. To obtain an estimate of total suspended solids, calculate the difference between total dissolved solids and total solids.

b. Interferences: See Section 2540A.2 and Section 2540B.1. Exclude large floating particles or submerged agglomerates of non homogeneous materials from the sample if it is determined that their inclusion is not representative. Because excessive residue on the filter may form a water-entrapping crust, limit the sample size to that yielding no more than 200 mg residue. For samples high in dissolved solids thoroughly wash the filter to ensure removal of dissolved material. Prolonged filtration times resulting from filter clogging may produce high results owing to increased colloidal materials captured on the clogged filter.

2. Apparatus

Apparatus listed in Section 2540B.2 and Section 2540C.2 is required, except for evaporating dishes, steam bath, and 180°C drying oven. In addition:

Aluminum weighing dishes.

3. Procedure

a. Preparation of glass-fiber filter disk: If pre-prepared glass fiber filter disks are used, eliminate this step. Insert disk with wrinkled side up in filtration apparatus. Apply vacuum and wash disk with three successive 20-mL portions of reagent-grade water. Continue suction to remove all traces of water, turn vacuum off, and discard washings. Remove filter from filtration apparatus and transfer to an inert aluminium weighing dish. If a Gooch crucible is used, remove crucible and filter combination. Dry in an oven at 103 to 105°C for 1 h. If volatile solids are to be measured, ignite at 550°C for 15 min in a muffle furnace. Cool in desiccators to balance temperature and weigh. Repeat cycle of drying or igniting, cooling, desiccating, and weighing until a constant weight is obtained or until weight change is less than 4% of the previous weighing or 0.5 mg, whichever is less. Store in desiccators until needed.

b. Selection of filter and sample sizes: Choose sample volume to yield between 2.5 and 200 mg dried residue. If volume filtered fails to meet minimum yield, increase sample volume up to 1 L. If complete filtration takes more than 10 min, increase filter diameter or decrease sample volume.

c. Sample analysis: Assemble filtering apparatus and filter and begin suction. Wet filter with a small volume of reagent-grade water to seat it. Stir sample with a magnetic stirrer at a speed to shear larger particles, if practical, to obtain a more uniform (preferably homogeneous) particle size. Centrifugal force may separate particles by size and density, resulting in poor precision when point of sample withdrawal is varied. While stirring, pipet a measured volume onto the seated glass-fiber filter. For homogeneous samples, pipet from the approximate midpoint of container but not in vortex. Choose a point both middepth and midway between wall and vortex. Wash filter with three successive 10-mL volumes of reagent-grade water, allowing complete drainage between washings, and continue suction for about 3 min after filtration is complete. Samples with high dissolved solids may require additional washings. Carefully remove filter from filtration apparatus and transfer to an aluminum weighing dish as a support. Alternatively, remove the crucible and filter combination from the crucible adapter if a Gooch crucible is used. Dry for at least 1 h at 103 to 105°C in an oven, cool in a desiccator to balance temperature, and weigh. Repeat the cycle of drying, cooling, desiccating, and weighing until a constant weight is obtained or until the weight change is less than 4% of the previous weight or 0.5 mg, whichever is less. Analyze at least 10% of all samples in duplicate. Duplicate determinations should agree within 5% of their average weight. If volatile solids are to be determined, treat the residue according to 2540E.

4. Calculation

$$\text{mg total suspended solids/L} = \frac{(A - B) \times 1000}{\text{sample volume, mL}}$$

where:

A = weight of filter + dried residue, mg, and
B = weight of filter, mg.

5. Precision

The standard deviation was 5.2 mg/L (coefficient of variation 33%) at 15 mg/L, 24 mg/L (10%) at 242 mg/L, and 13 mg/L (0.76%) at 1707 mg/L in studies by two analysts of four sets of 10 determinations each. Single-laboratory duplicate analyses of 50 samples of water and wastewater were made with a standard deviation of differences of 2.8 mg/L.

Appendix III – COD protocol

The COD analyses were performed with chemicals from the Spectroquant ® 114541 kit (Figure 1) by photometric method, with a Merck Spectroquant NOVA 60® photometer (Figure 2) and the thermo reactor used was a Merck Spectroquant TR620® (Figure 3). Readings are in mg/L.

Figure 1 - COD Spectroquant ® 114541 kit

Figure 2 - Merck Spectroquant NOVA 60® photometer

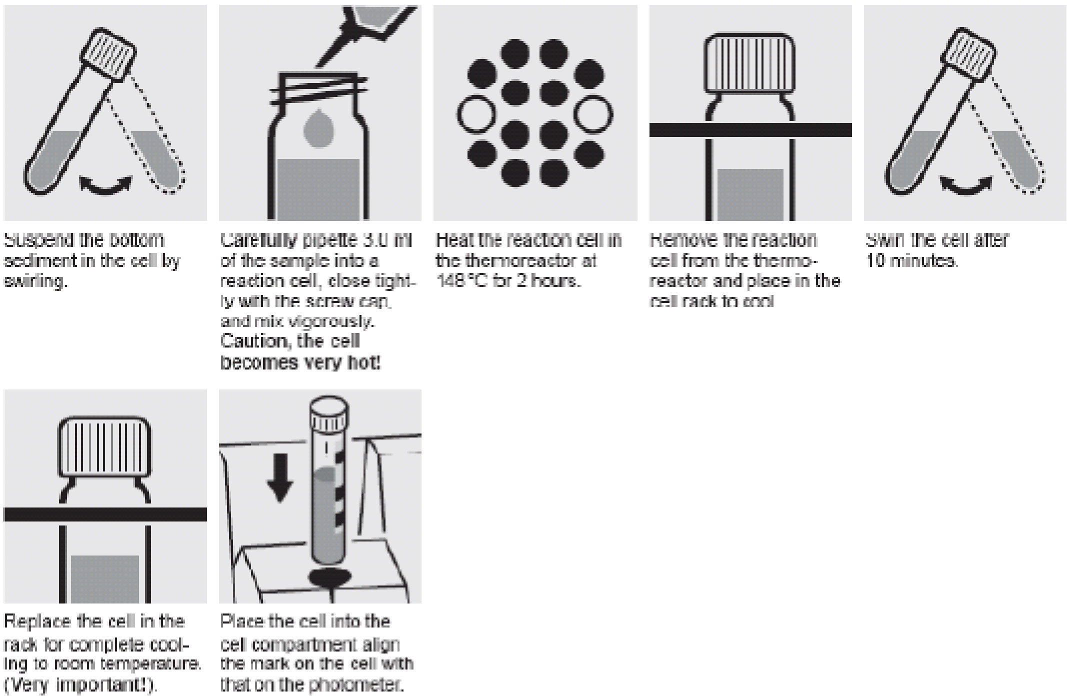
Figure 7 - Merck Spectroquant TR620® thermo reactor

Principle of the Merck COD Cell Tests:

• Measuring range: 25 – 1500 mg/L COD

Item no: 1.14541.

• Handling:



For more specific information visit Merck web site: http://www.merck-chemicals.com

Appendix IV – TOC protocol

TOC was measured with chemicals from a Spectroquant ® 114878 kit (Figure1) by photometric method with a Merck Spectroquant NOVA 60® photometer (Figure 2) and a Merck Spectroquant TR620 thermo reactor (Figure 3), with readings of the TOC value in mg/L.

Figure 1 - TOC Spectroquant ® 114878 kit

Figure 2 - Merck Spectroquant NOVA 60® photometer

Figure 7 - Merck Spectroquant TR620® thermo reactor

Principle of the Merck TOC Cell Tests:

• In a closed tube a water sample with dissolved organic matter is oxidised by means of potassium peroxo disulphate in acidic medium to form carbon dioxide.

• This penetrates through a special membrane and changes the colour of an indicator solution. The colour is measured as mg/l TOC after digestion and cooling to room temperature.

Removal of inorganic bound carbon (TIC):

Procedure for 1.14878.0001 5.0-80.0 mg/l	Place 25 ml of the sample into a suitable glass vessel.	Add 3 drops of **TOC-1K** and mix.	Check the pH, specified range pH < 2.5	Stir for 10 minutes.
1.14879.0001 50-800 mg/l means: in-build dilution step	Place 1.0 ml of the sample and 9.0 ml water (water for on-line analysis, art. 01051) into a suitable glass vessel.	Add 2 drops of **TOC-1K** and mix.	Check the pH, specified range pH < 2.5	Stir for 10 minutes.

Preparation of measurement sample:

Pipette 3.0 ml of stirred sample into a reaction cell.	Add 1 grey micro-spoonful of **TOC-2K**. **Immediately** close the cell tightly with an **aluminium cap** (art. 73500).	Heat the cell, standing on its head, at 120° C in the thermoreactor for 2 hours.	Let the cell, **standing on its head**, to cool for 1 hour.	Place the cell into the cell compartment with the vertical line facing the observer.

For more specific information visit Merck web site: http://www.merck-chemicals.com

Appendix V – Particle counter in range 0.4 -5.0 µm

For the particles counting determination the HIAC ChemShield MicroCount 100S Series particle counter was used, capable of measuring particles with a diameter in the range between 0.4 and 5.0µm (Clesceri *et al.*, 1998). Figure 1 and Figure 2 show a schematic representation of the particles counting set up and a picture, respectively.

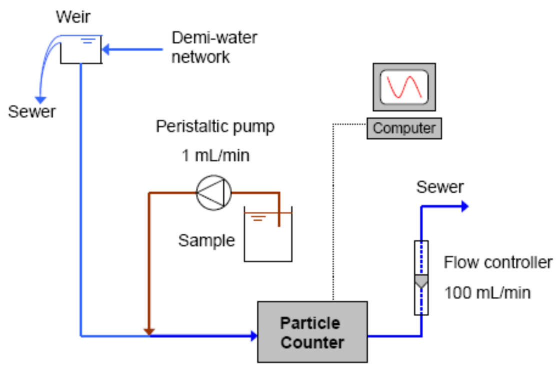


Figure 1 - Scheme of particles counter apparatus (Clesceri et al., 1998)

Figure 2 - Particles counter instrument in the TU Delft water lab

The following particles counting analyses explanation was based in the description of Clesceri *et al.* (1998), mentioned by Geilvoet (2009) in The Delft Filtration Characterization method, assessing membrane bioreactors activated sludge filtration.

Because the amount of particles in activated sludge free water is higher than the measuring range of the particle counter, the samples are always diluted with demi-water. The power required to produce a flow through the particle counter is induced by the demi-water network in the lab and a weir. With a pinch valve the flow rate is adjusted to the required value of 100 mL/min.

A peristaltic pump adds the free water sample to the demi-water flow with a flow of 1 mL/min (dilution factor of 100) before entering the particle counter. After passing the particle counter the sample is discharged to the sewer.

The particles are measured as they pass by a light blocking sensor which counts the number of particles in the size range between 0.4 and 5.0µm. These data are processed with the software application Particle Vision Online. The initial output consists of the number of particles per mL for different size range intervals; see Figure 3 for an example of a typical measurement.

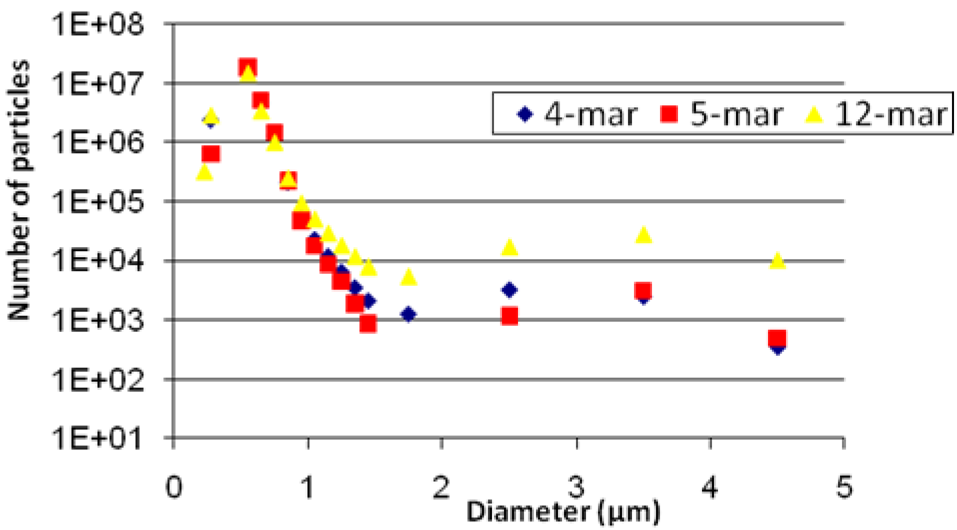


Figure 7 - Example of number of particles first output

As the particles shape is variable (Metcalf & Eddy, 2003), in this research all particles are assumed to be spherical and opaque. When the raw data are corrected for the demi-water flow the volume distribution can be calculated. Figure 4 represents the particles distribution for the cumulative volume data originating from Figure 5.

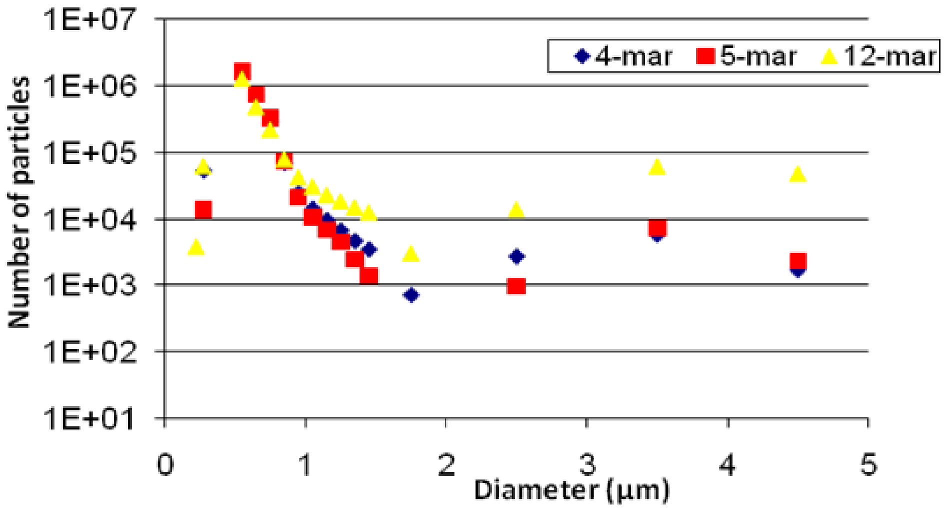


Figure 4 - Example of particles volume output

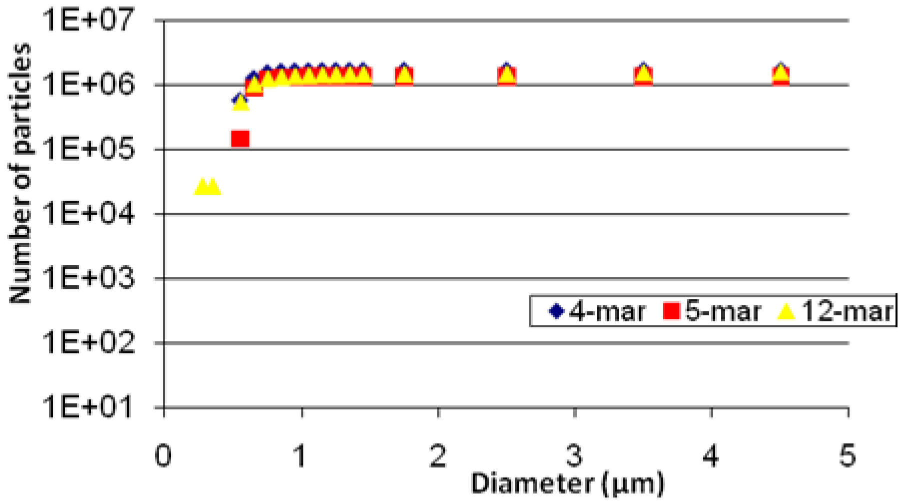


Figure 5 - Example of an output data for particles cumulative volume

Particles counting in range 0.4 - 5.0 µm, product details:

PERFORMANCE CHARACTERISTICS

MicroCount 100, 100S (0.1 µm Option)	
Sensitivity	0.1-5.0 µm @ 100 mL/min
Concentration Limit (10% optical coincidence)	100, 000 particles/mL
Flow Rate	100 mL/min (Typical); 200 mL/min (Maximum)
View Volume (% of flow sampled)	3% @ 150 mW
Light Source	150 mW (Typical) Near IR (837 nm) Laser Diode
Collection Optics	90° Light Scatter (0.1 µm to 0.4 µm) Near Forward Scatter (0.4 µm to 5.0 µm)
Maximum Operating Pressure	MicroCount 100 (uses quartz cell): 150 psi (1034 kPa) MicroCount 100S (uses sapphire cell): 75 psi (517 kPa)

OWER REQUIREMENTS (ALL SENSORS)

System Supplied	+5 Volts dc ±1% +15 Volts dc ±1% -15 Volts dc ±1%

PHYSICAL CHARACTERISTICS (ALL SENSORS)

Dimensions	15.2 cm (L) x 20.3 cm (W) x 10.7 cm (H) 6.0" x 8.0" x 4.2"
Weight	2.5 Kg (5.5 lbs)

ENVIRONMENT CHARACTERISTICS (ALL SENSORS)

Operating	7° - 45° C (44.6° - 113° F) 30 -95% Relative Humidity (non-condensing)
Non-operating	-40° - 71° C (-40° - 159.8° F) 0 -98% Relative Humidity (non-condensing)
Sample	7° - 45° C (44° - 113° F)

INPUT/OUTPUT

Electronic	
Counter & Signals	Standard DB-15 Connector
Mechanical	
Wetted Parts	Kel-F, Quartz, Sapphire (on 100S and 200S Sensors)
Seals	Kal-Rez
Purge Capability	0.125 in (3.2 mm) Hose barb Dry filtered nitrogen @ 15 psi (103 kPa) maximum
Sample In/Out Connections	
Liquid Sensors	0.25 in (6.36 mm) Flare-Tek fittings Teflon tubing